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**RAY T. BAYLESS, Editor**

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No. 3

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## HIGH TEMPERATURE PROPERTIES OF NICKEL-COBALT-IRON BASE AGE-HARDENING ALLOYS—PART II

BY CHARLES R. AUSTIN

### Abstract

*In Part II of this paper the behavior of the modified ternary alloys with respect to chemical corrosion in normal solutions of nitric and hydrochloric acids and to atmospheric corrosion at 800-1100 degrees Cent. (1470-2010 degrees Fahr.) is considered. It is shown that in general the alloys exhibit a markedly superior resistance to chemical corrosion in the reducing acid but that chemical attack is still progressive after 16 days of test. In the oxidizing acid the alloys containing chromium are attacked during the first 24 hours but thereafter very little loss in weight is observed.*

*At elevated temperatures data on weight loss have been presented in tabulated and graphical form, whereby direct comparison may be drawn between the behavior of the new alloys and commercial 80:20 nickel-chromium and stainless 18-8 steel. The importance of chromium is at once apparent. Many of the alloys have a greater resistance to high temperature oxidation than 18-8 steel, but at 1100 degrees Cent. (2010 degrees Fahr.) only the alloys containing aluminum are equal or superior to nickel-chromium.*

*The nature of the microstructure of the alloys has been illustrated and discussed, and data on the electrical resistivity of many of the alloys have been recorded.*

### RESISTANCE TO HIGH TEMPERATURE OXIDATION AND TO CHEMICAL CORROSION WITH ELECTRICAL RESISTIVITY AND METALLOGRAPHIC DATA ON THE ALLOYS

**I**N THE introduction to Part I of this investigation the general scope of the work was outlined, and data were presented on the mechanical, age-hardening, work-hardening and temperature-softening properties of the alloys. While these properties are important in a consideration of possible high temperature service it is frequently

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The author, Charles R. Austin, is associate professor of metallurgy, Pennsylvania State College, State College, Pa. Part I of this paper appeared in the June 1936 issue of *TRANSACTIONS*.

of equal importance to have information on their resistance to oxidation at elevated temperatures or to chemical corrosion.

The present paper serves to indicate the reactions of several of the alloys previously considered to prolonged oxidizing conditions at temperatures from 800 to 1100 degrees Cent. (1470-2010 degrees Fahr.). The resistance to chemical corrosion was studied at room temperature by the intermittent corrosion test using normal solutions of hydrochloric and nitric acid. On account of the possible interest in their application for electrical purposes, data on electrical resistivity are included. The results of some metallographic studies are also presented in order to indicate the microstructural nature of the alloys.

#### *Chemical Corrosion Tests*

The corrosion of the alloys was conducted in nitric and hydrochloric acids as it was considered that such tests would furnish information on their general corrosion resistance to oxidizing and reducing acids. The strength of the acid used was normal, 63 grams  $\text{HNO}_3$  per litre and 36.5 grams  $\text{HCl}$  per litre of water. The type of immersion test was similar to that used by Rawdon,<sup>11</sup> the specimens being submerged in acid for one minute and then suspended in air for one minute. The modifications which permitted temperature control for the corrosive liquid containers have been described by Hensel and Williams.<sup>12</sup>

The specimens selected were cut 2 inches long from round rolled bar, and were sand-blasted to insure uniformity in the nature of the surface tested. The specimens were placed in the machine on glass hangers and the tests run for 24 hours. They were then removed, washed, dried and weighed. This was followed by a second 1 day run, then 2 and 4 day periods of test and finally 8 days, the specimens being weighed at the end of each period.

The experimental data for the two series of tests are recorded in Tables IX and X. The alloys have been listed in order of merit, the alloy at the top of the table exhibiting the greatest resistance to chemical attack as revealed by loss in weight due to solution. Although all specimens were 2 inches long, variation in diameter ren-

<sup>11</sup>H. S. Rawdon, A. I. Kryniitsky and W. H. Finkeldey, "Types of Apparatus used in Testing the Corrodibility of Metals," *Proceedings, American Society for Testing Materials*, Vol. 24, Pt. II, 1924, p. 715-34.

<sup>12</sup>F. R. Hensel and C. S. Williams, "Corrosion Tests of Weld Deposits," *Metals and Alloys*, Vol. 5, Pt. I, Jan. 1934, p. 11.

Table IX  
Results of Intermittent Type Corrosion Tests in Normal Hydrochloric Acid

Merit Order	Original Wt.	Area Sq. Cm.	Days	Days	Days	Wt. Loss	Total Wt.	Synthetic Analysis				Type of Alloy	Merit Order	HNO <sub>3</sub> Merit Order								
														1	2	4	8					
														Alloy No.	Alloy No.	Alloy No.	Alloy No.					
1.	27.223	15.4	0.112	0.072	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	2913	56	30	7.5	2.5	4 Mo	Cr in K42B	18		
2.	42.666	19.8	0.115	0.090	0.081	0.142	0.386	0.814	0.0411	0.114	0.302	0.634	0.0417	3111	46	22	7.5	2.5	4 Mo	Cr in K42B	2	
3.	26.319	15.2	0.081	0.072	0.065	0.114	0.302	0.634	0.0417	0.114	0.302	0.634	0.0417	2912	53	29	7.5	2.5	8 Mo	Cr in K42B	16	
4.	24.693	14.8	0.085	0.075	0.070	0.065	0.135	0.261	0.632	0.0427	0.114	0.302	0.634	0.0427	2916	44	24	7.5	2.5	17 Cr	K42B + 5 Mo	2
5.	38.195	19.2	0.114	0.071	0.080	0.195	0.405	0.865	0.0450	0.114	0.302	0.634	0.0450	3115	56	30	7.5	2.5	4 Mo	Cr in K42B + Al	19	
6.	19.940	13.0	0.145	0.099	0.102	0.161	0.222	0.729	0.0561	0.222	0.161	0.222	0.0561	2909	56	30	7.5	2.5	4 Mo	Cr in K42B + Al	5	
7.	26.120	15.2	0.144	0.080	0.086	0.204	0.486	1.000	0.0658	0.204	0.086	0.204	0.0658	2914	30	58	10	2	4 W	Cr in K42B	6	
8.	46.730	20.2	0.122	0.117	0.171	0.371	0.600	1.111	0.611	0.171	0.371	0.600	0.611	3109	49	26	9	3	12 V <sub>a</sub>	(2907) 13 W for Cr in K42B	7	
9.	40.230	20.2	0.130	0.105	0.160	0.356	0.752	1.503	0.743	0.130	0.356	0.752	0.743	3113	46	25	7.5	2.5	19 Cr	K42B + Al	8	
10.	24.787	16.4	0.125	0.1	0.14	0.169	0.305	0.605	0.138	0.169	0.305	0.605	0.138	3009	44	24	7.5	2.5	17 Cr	(2910) K42B + 5 W	9	
11.	24.600	15.9	0.165	0.145	0.165	0.255	0.453	0.878	1.876	0.125	0.255	0.453	0.878	3006	47	30	7.5	2.5	13 Cr	K42B minus Ti	10	
12.	19.370	13.3	0.163	0.132	0.132	0.231	0.447	0.831	1.804	0.136	0.231	0.447	0.831	2870	48	25	7.5	2.5	20 Cr	K42B minus Ti	11	
13.	37.634	19.0	0.230	0.212	0.282	0.551	1.328	2.603	0.137	0.212	0.282	0.551	1.328	3107	23	47	7.5	2.5	20 Cr	(2869) High Co:Ni in K42B	12	
14.	57.665	22.6	0.364	0.271	0.375	0.723	1.351	3.064	0.138	0.271	0.375	0.723	1.351	3005	58	32	7.5	2.5	20 Cr	Commercial Pure Nickel	13	
15.	27.372	15.3	0.224	0.117	0.262	0.518	0.941	2.122	0.139	0.224	0.262	0.518	0.941	2867	27	54	15	4	20 Cr	K41B with high Co:Ni	14	
16.	15.886	12.2	0.190	0.155	0.239	0.385	0.743	1.712	0.120	0.190	0.239	0.385	0.743	2866	73	17	7.5	2.5	20 Cr	K41B with high Co:Ni	15	
17.	27.885	15.2	0.257	0.155	0.281	0.529	0.899	2.121	0.140	0.257	0.155	0.281	0.529	2915	30	50	10	2	V <sub>a</sub>	"Konal"	16	
18.	19.553	13.0	0.129	0.136	0.243	0.503	0.911	1.922	0.148	0.129	0.136	0.243	0.503	2868	26	54	7.5	2.5	10 Cr	"Konal"	17	
19.	19.212	13.1	0.155	0.129	0.136	0.243	0.503	0.911	1.922	0.154	0.129	0.136	0.243	0.503	2908	40	41	16.5	2.5	10 Cr	K41B with high Co:Ni	18
20.	33.668	16.5	0.242	0.186	0.376	0.711	1.299	2.814	0.170	0.242	0.186	0.376	0.711	2868	40	41	16.5	2.5	10 Cr	Commercial Pure Cobalt	19	
21.	24.495	14.8	0.218	0.186	0.233	0.394	0.759	1.715	0.175	0.218	0.186	0.233	0.394	2904	80	27	10.5	4.5	20 Cr	K52	20	
22.	35.204	18.0	0.217	0.176	0.377	0.774	1.545	3.129	0.178	0.217	0.176	0.377	0.774	3004	58	27	10.5	4.5	20 Cr	Commercial Ni-Cr	21	
23.	26.222	15.4	0.256	0.186	0.271	0.650	1.429	2.792	0.181	0.256	0.186	0.271	0.650	2908	15	40	42.5	2.5	20 Cr	K32	22	
24.	23.977	15.0	0.257	0.185	0.411	0.631	1.291	2.775	0.185	0.257	0.185	0.411	0.631	3008	24	24	42.5	2.5	20 Cr	K56	23	

Table X  
Results of Intermittent Type Corrosion Tests in Normal Nitric Acid

\*Total duration of test was 6 days (†2 day test)  
\*\*Total duration of test was 3 days (††1 day test)

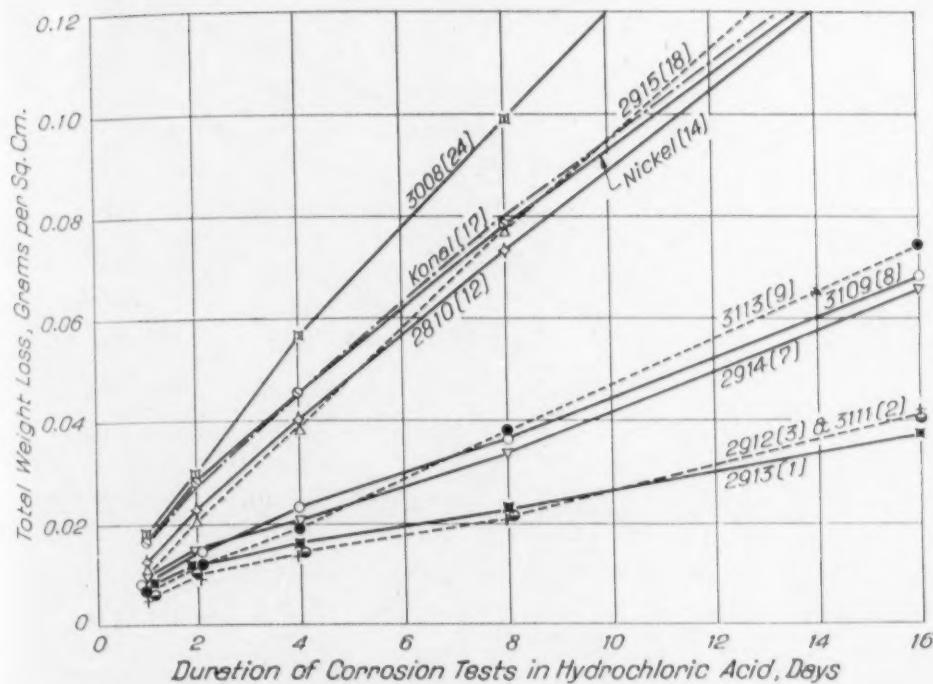


Fig. 9—Relation Between Weight Loss in Grams Per Square Centimeter and Duration of Test for Normal Hydrochloric Acid.

dered necessary calculation of superficial area exposed. Accordingly the original weight, area in square centimeters, and absolute weight loss after each test have been recorded, but the merit order has been taken from total weight loss per square centimeter after 16 days of test. The chemical analyses and characteristic composition feature are also appended.

The weight loss in grams per square centimeter has been calculated for several of the alloys and plotted against duration of test in Figs. 9 and 10 for hydrochloric and nitric acid respectively. Much wider variations appear in the nitric acid tests and attention should be drawn to the fact that the values plotted as weight loss in the ordinate used in the  $HNO_3$  graph, are ten times those used in plotting the data for HCl. However, a similar open scale has also been prepared for nitric acid (Fig. 11).

Correlating the position of the weight loss-time curves in Fig. 9 with the data in Table IX, it will be noted that the three alloys, 2913, 2912 and 3111, which have the maximum resistance to corrosion in hydrochloric acid, all contain molybdenum. These data represent the corrosion effect of substituting varying amounts of molyb-

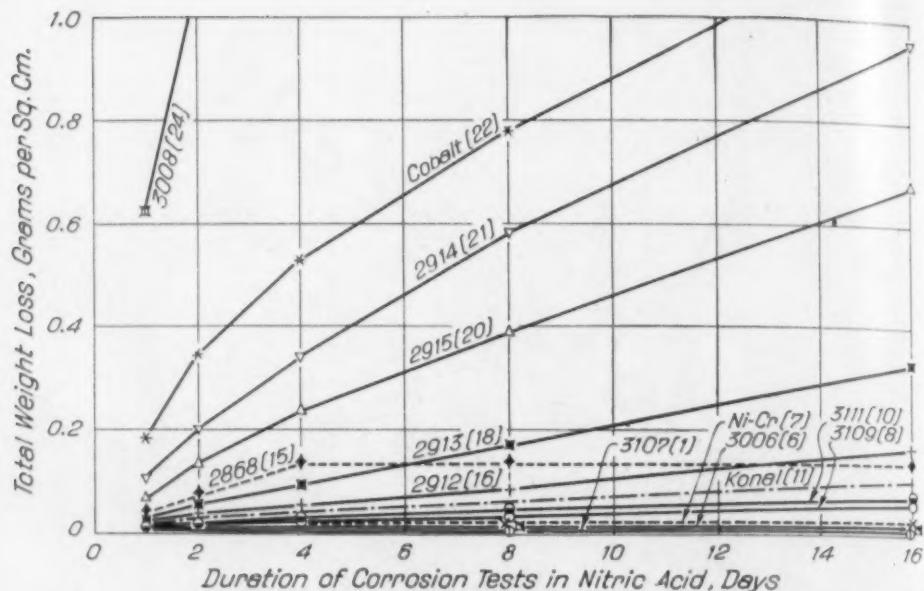


Fig. 10—Relation Between Weight Loss in Grams Per Square Centimeter and Duration of Test for Normal Nitric Acid.

denum for the 19 per cent chromium in K42B. Evidently the increase from 4 per cent (2913) to 19 per cent molybdenum (3111) has little effect in changing the corrosion resistance. Substitution of tungsten for chromium or the addition of tungsten to K42B appears to render the alloy less resistant to attack. A similar interference appears justified for aluminum additions. All these alloys have greater resistance to hydrochloric acid corrosion than has pure nickel. Increasing the cobalt content further decreases the resistance and nickel-chromium is surprisingly low in the series. It also appears interesting to record that the vanadium-bearing alloy with high cobalt holds position 7 in the merit order. The addition of 8 per cent chromium to this 2 per cent vanadium alloy (2914) results in the merit order number being reduced to 18 (Alloy 2915). It should be noted that the maximum solution corrosion is only five times the minimum corrosion in this series of tests.

In the nitric acid tests the variation is considerably greater, the best alloy possessing several thousand times the corrosion resistance of the poorest alloy. The chromium-bearing alloys exhibit the maximum resistance to corrosion and Fig. 11 shows that we have a series of alloys which no longer are subject to progressive corrosion as was the case with all alloys in the hydrochloric acid tests. Down to and including nickel-chromium with merit order number 7, practically all

the corrosion occurs during the first 24 hours. Beyond this period further solution is almost negligible.

Further correlation of Table X with Fig. 11 shows that a profound change occurs in corrosion characteristics when tungsten (3109 and 2909) and molybdenum (3111) are substituted for chromium. Nickel and cobalt are found respectively in the middle and near the

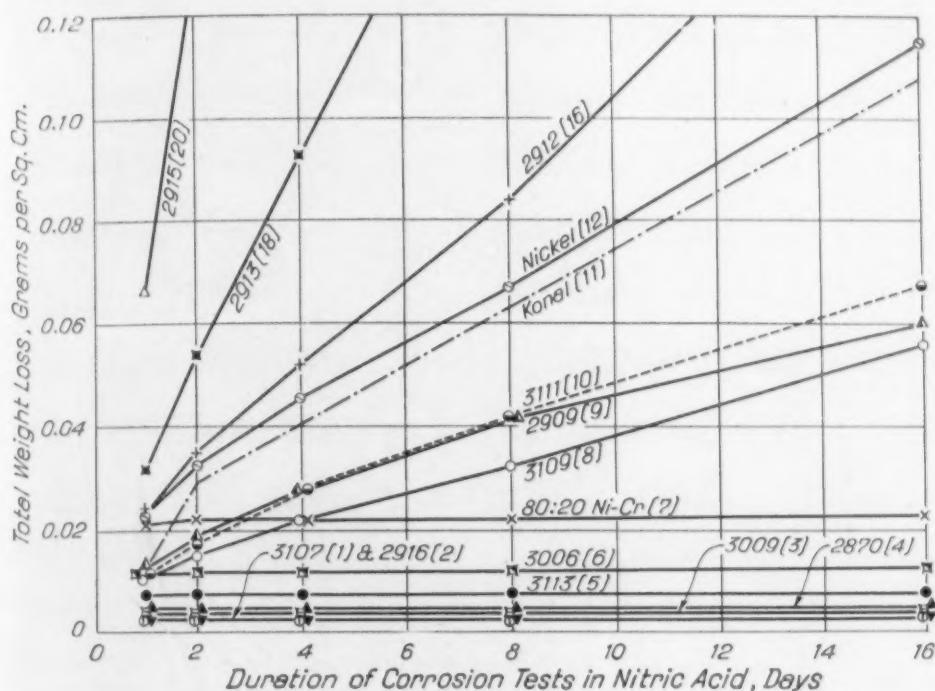


Fig. 11—Relation Between Weight Loss in Grams Per Square Centimeter and Duration of Test for Normal Nitric Acid Shown on a Scale Similar to That Used for the Hydrochloric Acid Tests.

bottom of the order of merit and in positions very similar to those for the hydrochloric acid tests.

High ratio of cobalt to nickel content reacts unfavorably (compare the medium chromium alloys of merit order 6 and 15) and 8 and 4 per cent substitution of molybdenum for 19 per cent chromium brings the alloy low down in the table. The addition of aluminum to the 4 per cent molybdenum alloy doubles the rate of solution of the alloy (2913 and 3115). Both the vanadium alloys exhibit poor resistance to nitric acid corrosion. The high cobalt, high iron alloy (K56) holds bottom place in both series of tests.

After the conclusion of the corrosion tests a study of the nature of the corroded surface was made. The general appearance is difficult

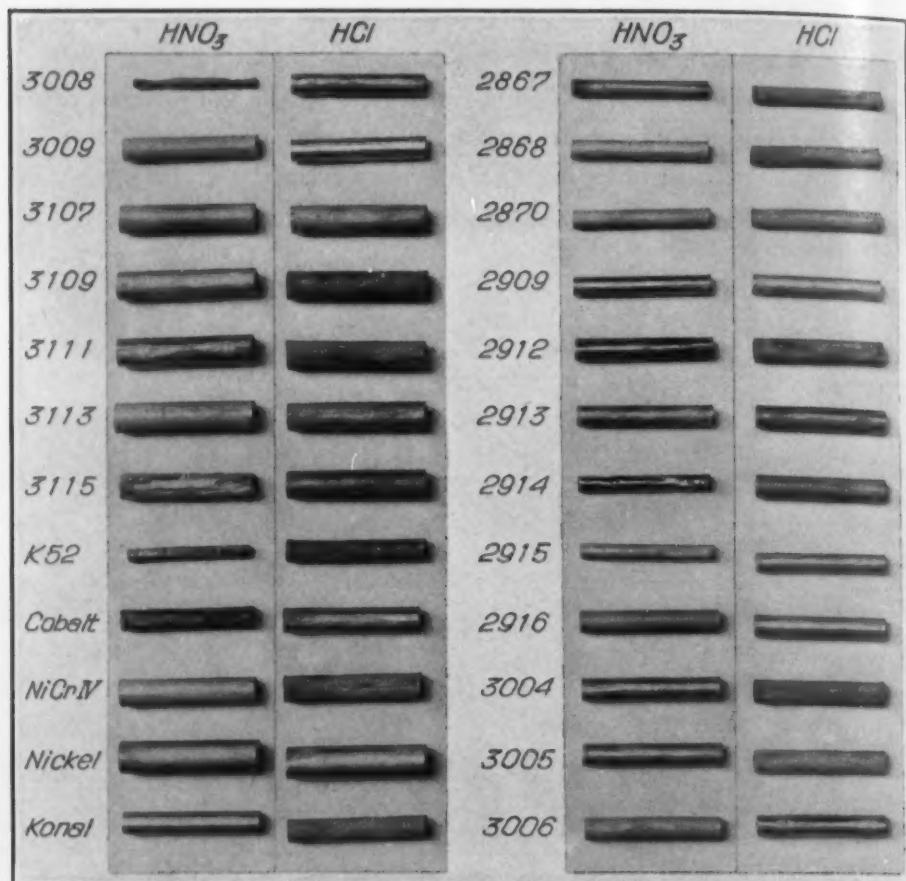


Fig. 12—Appearance of Test Samples After Chemical Corrosion Tests in Hydrochloric and Nitric Acid.

to photograph but a fair reproduction is presented in Fig. 12. The identification numbers refer to the two specimens immediately to the right.

Cobalt showed the maximum selective corrosion in both series of tests. The corrosion of nickel and "Konal" was uniform. Nickel-chromium exhibited the development of "corrosion cracks" parallel with the direction of rolling in the hydrochloric acid test. The development of "corrosion cracks" was common in this test and can be related to the high cobalt alloys and to those containing molybdenum. One high ferrotitanium alloy (3004-K32) shows this characteristic to a marked degree.

In the nitric acid series pronounced selective attack is found in both the vanadium alloys (2914 and 2915) and particularly in the molybdenum alloy containing aluminum (3115).

## ATMOSPHERIC CORROSION AT ELEVATED TEMPERATURES

Much attention during recent years has been devoted to studies of the mechanism of oxidation of metals and to the effect of time, temperature and alloying element on the amount and nature of the oxidation. In his important paper on heat-resisting steels Hatfield<sup>13</sup> included many references to the subject and more recently Rickett and Wood<sup>14</sup> extended the bibliography.

In the present investigation the purpose was to examine the relative resistance of the alloys to atmospheric oxidation at temperatures above 800 degrees Cent. (1470 degrees Fahr.) and to compare the results with data obtained under similar conditions on well known metals and commercial high temperature alloys. The total number of materials tested was thirty, and the tests were run for 100, 200 and 400 hours at 800, 900, 1000 and 1100 degrees Cent. (1470, 1650, 1830, 2010 degrees Fahr.).

Of the methods used for evaluating resistance to oxidation probably none is entirely satisfactory, and on account of the large number of alloys in the present work it was decided to use the simple loss of weight method. Two important factors must be considered in oxidation tests—resistance to oxidation per se and tendency to scale. All but the noble metals oxidize and hence the nature of the scale formed is of paramount importance. With some alloys the scale appears to be relatively tenacious only when a constant temperature is maintained. Others do not appear so susceptible to temperature changes.

In an attempt to incorporate the temperature change effect in the present series of tests the alloys were heated and cooled three times for each test temperature. When cool the samples were jarred by tapping in order to remove any loose scale, so that it might be possible to differentiate between a loose and truly adherent scale.

#### Method of Test

The specimens, cut in duplicate, 3 inches long from forged strips  $\frac{7}{8}$ -inch wide by  $\frac{5}{16}$ -inch thick, had an average weight of about 50 grams, and a total superficial area of 42 square centimeters. After

<sup>13</sup>W. H. Hatfield, "Heat Resisting Steels," *Journal, Iron and Steel Inst.*, 1927, I, p. 483.

<sup>14</sup>R. L. Rickett and W. P. Wood, "The Action of Oxygen and Hydrogen Sulphide Upon Iron-Chromium Alloys at High Temperatures," *TRANSACTIONS, American Society for Metals*, Vol. 22, 1934, p. 347.

sand blasting, a  $\frac{5}{16}$ -inch hole was drilled near the top of the sample. The strips were then hung on refractory rods arranged in 4 rows and supported by end bricks as shown in Fig. 13. This picture illustrates the experimental conditions at the end of the final run at 1100 degrees Cent. (2010 degrees Fahr.) by which time severe oxidation in previous tests had reduced the number of specimens worthy

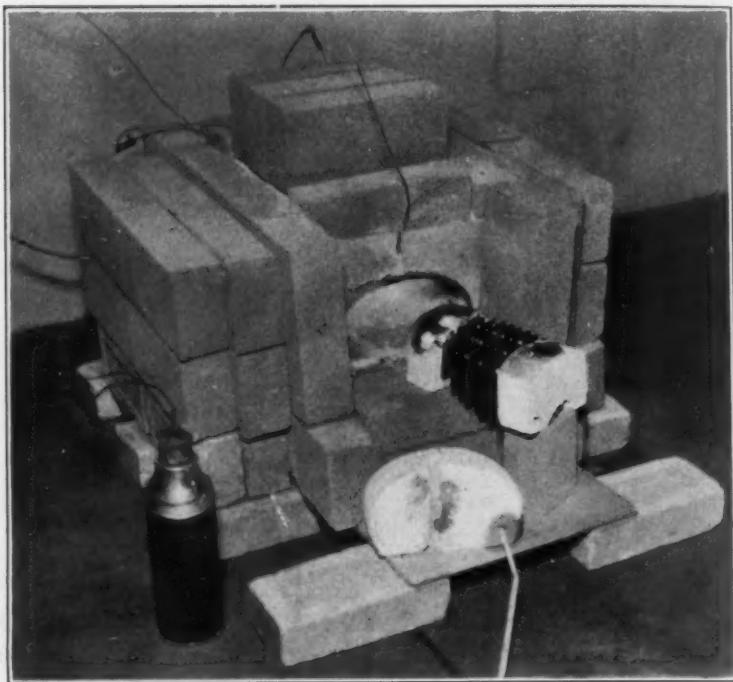


Fig. 13—Experimental Method of Conducting Oxidation Tests to Determine Resistance to Atmospheric Corrosion at 800, 900, 1000 and 1100 Degrees Cent.

of test to fourteen. The first two rows (Fig. 13) contain Series I in the order listed in Tables XI to XIV, and the second two rows are the duplicate series arranged in the furnace in reverse order to the alloy numbers listed.

The furnace muffle was heated by use of nickel-chromium resistance wire. Suitable distribution of the winding with the addition of heating units in the end bricks permitted a uniform temperature ( $\pm$  5 degrees Cent.) over the entire test area. The oxidizing atmosphere was air. The bricks closing the front and back of the furnace fitted loosely in order that air might readily diffuse through the muffle and thus maintain the normal oxygen concentration. The specimens were placed in the furnace while at temperature and removed im-

Table XI  
Oxidation Tests at 800 Degrees Cent. Results Expressed as Total Weight (in Grams)  
Gain or Loss for 100, 200 and 400 Hours Duration of Test

Alloy 2867	Tests at 800° Cent.										Rockwell "C" Scale 35	
	100 Hours		200 Hours		400 Hours							
	Gain	Loss	Gain	Loss	Gain	Loss						
		.386	90 s.		.699	70 s.						
2868	.075		c.a.	.087		c.a.	.098				12	
2870	.015		c.a.	.020		c.a.	.021				18-22	
2908		.483	c.s.		.390	c.a.		.866	c.s.		30	
2909		.482	c.s.		.390	c.a.		1.090	90 s.		13-19	
2912	.082	60 s.		.470	90 s.		1.117	c.s.			24	
2913	.450	c.s.		.864	95 s.		1.573	c.s.			13-19	
		.456	90 s.		.196	c.a.		1.452	75 s.		— 9	
2914							0.003	....	c.a.			
2915	.129		c.a.	.202		c.a.	.240		c.a.		— 2	
2916	.020		c.a.	.028		c.a.	.034		c.a.		22	
2920	.118		c.a.	.155		c.a.	.194		c.a.		— 14	
		.008	90 a.	....	.030	90 a.		.246	85 a.		37	
3004	.154		95 a.	.141	....	c.a.		.474	c.s.			
		.449	90 s.		.556	90 a.		1.251	65 s.		25	
3006	.035		c.a.	.045		c.a.	.051		c.a.		25	
3007	.019		c.a.	.025		c.a.	.030		c.a.		29	
		....	1.062	c.s.	....	.822	c.a.		.500	c.a.	37	
3008	.307	....	c.a.	....	.777	65 s.		.450				
		.022		c.a.	.027		c.a.	.034		c.a.	28	
18-8		.085	c.s.		.215	c.s.		.342	c.s.		— 3	
3107	.020		c.a.	.027		c.a.	.032		c.a.		30	
3108	.008		c.a.	.011		c.a.	.015		c.a.		43	
		....	.243	c.s.	....	.153	c.a.		.614	50 s.	36	
3109	.148	....	c.a.	.171	....	c.a.	.009		50 s.			
		.180	75 s.		.620	c.s.		1.410	c.s.		36	
3111			c.a.	.021		c.a.	.025		c.a.		38	
3113	.016		c.a.	.015		c.a.	.019		c.a.		43	
		.169	....	95 a.	.196		c.a.	.260		95 a.	37	
3115	.198	....				10 s.	.179		c.a.			
K52		.394	c.s.		.242	c.a.		.916	c.s.		34	
Cobalt		4.290	c.s.		8.136	c.s.		18.07	c.s.		0	
Nickel	.084		c.a.	.120		c.a.	.171		c.a.		— 30	
Ni Cr IV	.017		c.a.	.022		c.a.	.025		c.a.		12-16	
Konal	.140		c.a.	.140		90 a.		.407	50 s.		— 3	

mediately at the end of the run. This facilitated the removal of scale which was less adherent, and constituted a more severe oxidation test procedure.

The first tests were run at 800 degrees Cent. (1470 degrees Fahr.). After 100 hours the samples were removed, air-cooled, and

**Table XII**  
**Oxidation Tests at 900 Degrees Cent. Results Expressed as Total Weight (in Grams)**  
**Gain or Loss for 100, 200 and 400 Hours Duration of Test**

Alloy	Tests at 900° Cent.								Rockwell "C" Scale	
	100 Hours		200 Hours		400 Hours					
	Gain	Loss	Gain	Loss	Gain	Loss	c.s.	c.s.		
2867		1.327		c.s.		2.559		c.s.	36	
2868	...	.230	60 a.		0.797	80 a.		2.05	70 a.	
	.046	....	90 a.		1.119	30 a.		3.20	10 a.	
2870	.021		c.a.	.031		c.a.	0.032		11-15	
2908		1.363	c.s.		3.53	c.s.		6.29	c.s.	
2909	.121	....	90 a.		2.82	c.s.		5.12	c.s.	
	.159		75 a.						15	
2912		1.208	c.s.		2.53	c.s.		4.73	c.s.	
2913		1.474	c.s.		3.08	c.s.		5.61	c.s.	
2914	....	2.623	90 s.		6.6	c.s.		13.4	c.s.	
	1.063	....	c.a.						-19	
2915		2.144	c.s.		4.70	95 s.		9.35	c.s.	
2916	0.014		c.a.		.012	c.a.		.047		
2920	.109		c.a.	129		c.a.	.058		c.a.	
3004		.833	c.s.		1.932	c.s.		3.93	c.s.	
3005		.739	50 s.		3.6	c.s.		6.76	c.s.	
		1.644	c.s.						25	
3006		.024	c.a.	0.007		c.a.	0.029	0.040		
				0.076					31	
3007		.018	c.a.		0.059	c.a.		0.112		
3008		.321	c.a.		2.217	c.s.		1.51		
		.113	60 a.		1.801	90 s.		1.44	c.a.	
3009		.026	c.a.		0.029			0.065		
18-8		.798	c.s.		0.941	30 a.		1.087		
					1.623	c.s.		2.324	c.s.	
									-6	
3107	.008		c.a.		0.045	c.a.		0.071		
3108	.015		c.a.	0.025		c.a.	0.031		c.a.	
3109		.965	c.s.		2.296	c.s.		4.67	c.s.	
3111		.881	c.s.		1.93	c.s.		3.95	c.s.	
3113	.025		c.a.	0.039		c.a.	0.039		c.a.	
3114	.014		c.a.	0.023		c.a.	0.028		c.a.	
3115		.809	c.s.		1.78	c.s.		3.46	c.s.	
K52		1.263	c.s.		2.60	c.s.		3.9	c.s.	
Cobalt					No Test Data					
Nickel	.222		c.a.	0.358		c.a.	0.511		c.a.	
Ni Cr IV	.017		c.a.	0.025		c.a.	0.031		c.a.	
Konal		1.075	c.s.		2.435	c.s.		4.67	c.s.	
									-6	

any scale that was easily removed was knocked from the specimens. The gain or loss in weight was recorded and the specimens arranged in order on the refractory rods and placed in the hot furnace for a second 100 hours. Weighings were again taken after the procedure recorded and the total change from initial weight observed. Again

(In Grams)

	Rockwell "C" Scale	
s.	36	
0 a.		
0 a.	4	
s.	11-15	
s.	29	
s.	15	
s.	16	
s.	9	
s.	-19	
s.	-9	
	19	
s.	-16	
s.	37	
s.	25	
	31	
	32	
	34	
	33	
-	6	
34		
40		
35		
36		
33		
42		
33		
31		
-29		
8		
-6		

Table XIII  
Oxidation Tests at 1000 Degrees Cent. Results Expressed as Total Weight (in Grams)  
Gain or Loss for 100, 200 and 400 Hours Duration of Test

Alloy	Tests at 1000° Cent.									Rockwell "C" Scale	
	100 Hours			200 Hours			400 Hours				
	Gain	Loss	Scale	Gain	Loss	Scale	Gain	Loss	Scale		
2867	2.666	c.s.		6.364	c.s.		11.634	c.s.		23	
2868	0.960	75 a.		2.592	10 s.		4.457	c.s.	-10		
	0.659	50 s.		2.383			3.352	90 s.			
2870	0.302	c.a.		0.399	c.a.		0.518	c.s.	0		
2908	4.025	c.s.		6.741	c.s.		11.14	c.s.	17		
2909	4.43	c.s.		7.514	c.s.		12.29	c.s.	-1		
2912	3.27	c.s.		5.693	c.s.		9.17	c.s.	7		
2913	4.38	c.s.		7.205	c.s.		11.40	c.s.	-2		
2914	10.23	c.s.		17.21	c.s.						
2915	6.45	c.s.		11.51	c.s.		18.33	c.s.	-15		
2916	0.245	c.s.		0.676	c.s.		0.881	c.s.	6		
2920	0.780	65 a.		2.16	80 s.		3.123	80 s.	-35		
	1.487	90 a.		2.50	90 s.		3.994				
3004	2.76	c.s.		4.97	c.s.		8.863	c.s.	22		
3005	4.31	c.s.		7.54	c.s.		12.40	c.s.	13		
3006	0.612	c.s.		2.316	c.s.		2.611	c.s.			
	0.308	c.s.		0.677			1.517	90 s.	15		
3007	0.41	c.s.		0.73	c.s.		1.241	c.s.	21		
3008	3.238	c.s.		3.14	30 s.		2.644		15		
	3.758			5.03	c.s.		5.233	20 s.			
(2910)	0.281	80 s.		0.58	80 s.		0.781	80 s.	26		
	0.253	50 s.		0.66	50 s.		0.906	60 s.			
18-8	2.52	c.s.		4.50	c.s.		4.637	c.s.	-13		
3107	0.50	50 s.		0.526	30 s.		1.173	90 s.	22		
	0.415	c.s.		1.975	c.s.		2.241	c.s.			
3108	0.007	c.a.	0				0.016	c.s.	34		
3109	3.37	c.s.		5.895	c.s.		9.537	c.s.	30		
3111	2.6	c.s.		4.985	c.s.		7.831	c.s.	27		
3113	0.13	90 a.		0.209	90 a.		0.320	c.s.	32		
3114	0.026	90 a.		0.040	90 a.		0.061	c.s.	37		
3115	2.57	c.s.		4.498	c.s.		7.47	c.s.	29		
K52	3.223	c.s.		6.219	c.s.		11.014	c.s.	17		
	3.49			6.694			10.803				
Cobalt			No	Test	Data						
Nickel	0.53	c.a.	0.699	c.a.	1.034	c.a.					
Ni Cr IV	0.158	90 a.	0.110		0.110	c.s.	-5				
	0.182	50 a.	0.116		0.106						
Konal	3.45	c.s.	5.50	c.s.	9.128	c.s.	-23				

the specimens were subjected to a further 200-hour test and the final total gain or loss in weight for 400 hours recorded. The complete data for 800 degrees Cent. (1470 degrees Fahr.) are recorded in Table XI. It will be noted that in some instances two values are

specimens.  
arranged  
ce for a  
rocedure  
Again

**Table XIV**  
**Oxidation Tests at 1100 Degrees Cent. Results Expressed as Total Weight (in Grams)**  
**Gain or Loss for 100, 200 and 400 Hours Duration of Test**

Alloy	Tests at 1100° Cent.				
	100 Hours		200 Hours		400 Hours
	Loss	Scale	Gain	Loss	Loss
2867	8.581	c.s.			
2868	2.731	c.s.		7.511	13.605
2870	0.483	95 s.		2.060	2.544
2908	6.480	c.s.			
2909	6.978	c.s.			
2912	4.808	c.s.		10.233	
2913	6.097	c.s.			
2914					
2915	10.774	c.s.			
	3.573	c.a.			
2916	0.724	50 s.		9.141	9.535
				6.820	7.214
2920	3.381	c.s.		11.221	
				9.021	
3004	5.111	30 s.		10.991	
3005	6.700	30 s.			
3006	1.964	c.s.		4.942	7.070
				3.650	5.778
3007	0.467	c.s.		1.361	2.565
				0.987	2.191
3008	3.245	c.s.		1.593	
				7.445	
(2910)	0.809	80 s.		2.240	4.065
18-8	1.247	c.s.	4.76*		
3107	0.592	c.s.		2.292	4.392
3108	0.007	c.s.		0.090	0.197
				0.509	0.562
3109	5.915	95 s.		15.578	
				18.820	
3111	4.788	c.s.		11.730	17.619
3113	0.233	c.s.		2.833	3.391
3114	0.010	c.s.		0.125	0.224
3115	4.079	c.s.		9.499	14.816
K52	7.435	c.s.			
Cobalt			No Test Data		
Nickel	+0.844	c.a.	1.284		+1.93
Ni Cr IV	0.076	c.s.		0.145	0.404
					0.359
Konal	6.625	80 s.			

\*Gain in weight was obviously due to gas attack from "transite" board used under specimen in this one series of tests.

recorded as the results of test on an alloy. Occasionally there was complete lack of agreement in the data obtained on duplicate tests. This was particularly evident when one specimen was found to

have a loose scale while the check specimen exhibited an adherent scale. In such case the behavior of both specimens is indicated.

However, in the large majority of tests, there was very close agreement between the duplicate specimens, and hence the mean of two similar results is given in the tables.

After the experiments at 800 degrees Cent. (1470 degrees Fahr.) the samples were cleaned by sand-blasting in order to maintain uniformity of surface at the start of a test. The hardness was then recorded and a similar series of three runs, up to a total of 400 hours, was conducted at 900 degrees Cent. (1650 degrees Fahr.). The data are presented in Table XII. Cobalt was the only metal not included in the higher temperature tests on account of its poor resistance to oxidation (see Table XI).

After again sand-blasting, a series of tests at 1000 degrees Cent. (1830 degrees Fahr.) was run. At the end of 400 hours at temperature the samples were furnace cooled. The Rockwell hardness values recorded in this series (Table XIII) therefore, indicate the effect of 400 hours at 1000 degrees Cent. followed by furnace-cooling and sand-blasting.

With the final series of oxidation tests at 1100 degrees Cent. (2010 degrees Fahr.) many of the alloys were so markedly oxidized that a selection was made for further test of those alloys which had shown relatively little weight change. Table XIV shows which alloys were too poor to permit further test. For the final run of 200 hours at 1100 degrees Cent. (2010 degrees Fahr.) only 14 of the 20 alloys merited this test.

An important modification in test procedure must be mentioned. For the second 100 hours at 1100 degrees Cent. (2010 degrees Fahr.) the specimens were hung on the refractory rods and the assembly placed on a "transite"\*\* board to facilitate introduction into the hot furnace. Evidently the "transite" as it heated up gave off gases which seriously corroded certain of the alloys, because many were much more seriously attacked, particularly at the lower end of the specimen, than had been the case in the first 100 hour duration of test.

Before testing at 1100 degrees Cent. (2010 degrees Fahr.) strips were cut from the base of all materials for metallographic examination, so that the area of specimen for the runs at 1100 degrees Cent. (2010 degrees Fahr.) was about 35 square centimeters.

\*An asbestos composition board.

## RESULTS OF OXIDATION TESTS

A general summary of the change in weight after 400 hours at each temperature is provided in Table XV. The alloys are listed in their order of merit for the 800 degrees Cent. test along with their chemical composition. Where duplicate tests gave appreciably different values the one indicating maximum corrosion attack was included in Table XV. The nature of the oxide scale is recorded in each of the tables by "c.a." completely adherent, "c.s." completely scaled or by a per cent adherent or scaled.

Reference to Table XV will show that in general the merit order for the alloys after the 900, 1000 and 1100 degrees Cent. (1650, 1830, 2010 degrees Fahr.) treatment is not materially changed from that established by the tests at 800 degrees Cent. (1470 degrees Fahr.). At 800 degrees Cent. exactly half the alloys gained weight and half lost weight due to scaling. The remarkable difference between the behavior of nickel and cobalt was hardly to be anticipated. Cobalt scaled so badly after 400 hours at 800 degrees Cent. (1470 degrees Fahr.) that it was omitted from further test. All chromium alloys are found in the top half of the table where slight gain in weight was observed, with the exception of 18-8 stainless which lost weight. Loss in weight was obtained in all alloys where chromium had been substituted by varying amounts of molybdenum and tungsten in the K42B type alloy with the lone exception of 3115 containing 2.5 per cent aluminum.

After 400 hours at 900 degrees Cent. (1650 degrees Fahr.) only seven alloys gained weight. These included K42B with aluminum (3114) or without titanium (2870), nichrome and pure nickel. At 1000 degrees Cent. (1830 degrees Fahr.) it was surprising to find that nickel was the only metal to gain weight on account of its extremely adherent scale. Nickel still maintained its increase in weight at 1100 degrees Cent. (2010 degrees Fahr.) when most of the alloys tested began to scale badly. The only two alloys comparable with nichrome at the higher temperatures are the high aluminum alloys 3108 and 3114.

In an endeavor to reveal more clearly the oxidation characteristics of the alloys four figures have been prepared to correlate oxidation resistance with time and with temperature of test.

The behavior of several K42B modifications in comparison with "Konal," 18-8 and nichrome in the temperature range 800 to 1100

Table XV  
Summary of Data for Oxidation Tests Including Chemical Analysis and Merit Number of all the Metals  
and Alloys subjected to Test. The Values recorded indicate total change in weight  
in Grams after 400 Hours

Alloy	Chemical Composition						Tests at 800° Cent.			Tests at 900° Cent.			Tests at 1000° Cent.			Tests at 1100° Cent.		
	Ni	Co	Fe	Ti	Cr	Al	Merit No.	Weight Change	Merit No.	Weight Change	Merit No.	Weight Change	Merit No.	Weight Change	Merit No.	Weight Change		
3108	23	47	7.5	2.5	20	Cr 5 Al	1	c.a.	+0.015	2	c.s.	+0.031	2	c.s.	-0.016	4	-0.562	
3114	46	25	7.5	2.5	19	Cr 5 Al	2	c.a.	+0.019	1	c.a.	+0.028	3	c.s.	-0.061	2	-0.224	
2870	48	25	7	...	20	Cr	3	c.a.	+0.021	4	c.a.	+0.032	6	c.s.	-0.518	5	-2.544	
NiCr IV	80	25	7.5	2.5	19	Cr 2.5 Al	4	c.a.	+0.025	2	c.a.	+0.031	4	c.s.	-0.11	3	-0.404	
3113	46	25	7.5	2.5	19	Cr 2.5 Al	5	c.a.	+0.025	5	c.a.	+0.039	5	c.s.	-0.320	7	-3.391	
3007	45	25	7.5	2.5	20	Cr	6	c.a.	+0.030	12	c.a.	+0.112	9	c.s.	-1.241	6	-2.565	
3107	23	47	7.5	2.5	20	Cr	7	c.a.	+0.032	11	c.a.	+0.071	10	c.s.	-2.241	9	-4.392	
2916	44	24	7.5	2.5	17	Cr 5 Mo	8	c.a.	+0.034	9	c.a.	-0.047	7	c.s.	-0.881	11	-9.535	
3009	44	24	7.5	2.5	17	Cr 5 W	9	c.a.	+0.034	10	...	-0.065	8	60 s.	-0.906	8	-4.065	
3006	47	30	7.5	2.5	13	Cr	10	c.a.	+0.051	8	...	-0.033	11	c.s.	-2.611	10	-7.070	
2868	26	54	7.5	2.5	10	Cr	11	c.a.	+0.098	15	90 s.	-3.20	13	c.s.	-4.457	12	-13.605	
Nickel	77	20	...	3	Si	...	12	c.a.	+0.171	7	c.a.	+0.511	1	c.a.	+1.034	1	+1.93	
2920	30	50	10	...	8	Cr 2 Va	13	c.a.	+0.194	6	c.a.	-0.058	12	80 s.	-3.994	...	...	
2915	56	30	7.5	2.5	4	Mo 2.5 Al	14	c.a.	+0.240	28	c.s.	-9.35	28	c.s.	-18.33	...	2920	
3115	18	8	74	2.5	18	Cr	15	95 a.	+0.260	16	c.s.	-3.46	16	c.s.	-7.47	13	-14.816	
K-8	73	17	7.5	2.5	50	s.	16	c.s.	-0.342	14	c.s.	-2.324	14	c.s.	-4.637	...	18.8	
Konal	58	27	10.5	4.5	17	50 s.	18	c.s.	-0.407	20	c.s.	-4.67	19	c.s.	-9.128	...	Konal	
3008	15	40	42.5	2.5	18	c.s.	19	c.a.	-0.500	13	50 s.	-3.93	18	c.s.	-8.863	...	(K32)	
3109	49	26	7.5	2.5	15	W	20	c.s.	-0.614	20	c.s.	-4.51	15	90 s.	-5.233	...	(K56)	
2908	53	29	7.5	2.5	8	W	21	c.s.	-0.866	26	c.s.	-4.67	21	c.s.	-9.537	...	(2907)	
K52	40	41	16	2.5	90	s.	22	c.s.	-0.916	17	c.s.	-6.29	23	c.s.	-11.14	...	2908	
2909	56	30	7.5	2.5	4	W	23	c.s.	-1.090	23	c.s.	-3.9	22	c.s.	-11.014	...	K52	
2912	53	29	7.5	2.5	8	Mo	24	c.s.	-1.117	22	c.s.	-5.11	26	c.s.	-12.29	...	2909	
3005	58	32	7.5	2.5	25	65 s.	25	c.s.	-1.251	27	c.s.	-4.73	20	c.s.	-9.17	...	2912	
2867	27	54	15	4	26	70 s.	26	c.s.	-1.396	25	c.s.	-6.03	25	c.s.	-12.40	...	(K21)	
3111	46	25	7.5	2.5	19	Mo	27	c.s.	-1.410	19	c.s.	-3.95	17	c.s.	-11.634	...	(2867)	
2914	30	58	7.5	2.5	2	Va	28	c.s.	-1.452	29	c.s.	-13.4	29	c.s.	-7.831	14	-17.619	
2913	56	30	7.5	2.5	4	Mo	29	c.s.	-1.573	24	c.s.	-5.61	24	c.s.	-17.21*	...	(2911)	
Cobalt	...	...	...	...	30	c.s.	-18.071	30	...	...	...	...	30	-11.40	...	2914		
															...	...	2913	

\*200 Hours

degrees Cent. (1470-2010 degrees Fahr.) is well illustrated in Fig. 14. The results for both samples of alloy 3108 at 1100 degrees Cent. have been included. The marked difference in behavior of the two samples may be ascribed to the gaseous corrosion medium given off by the "transite" board. Thus after 100 hours the weight

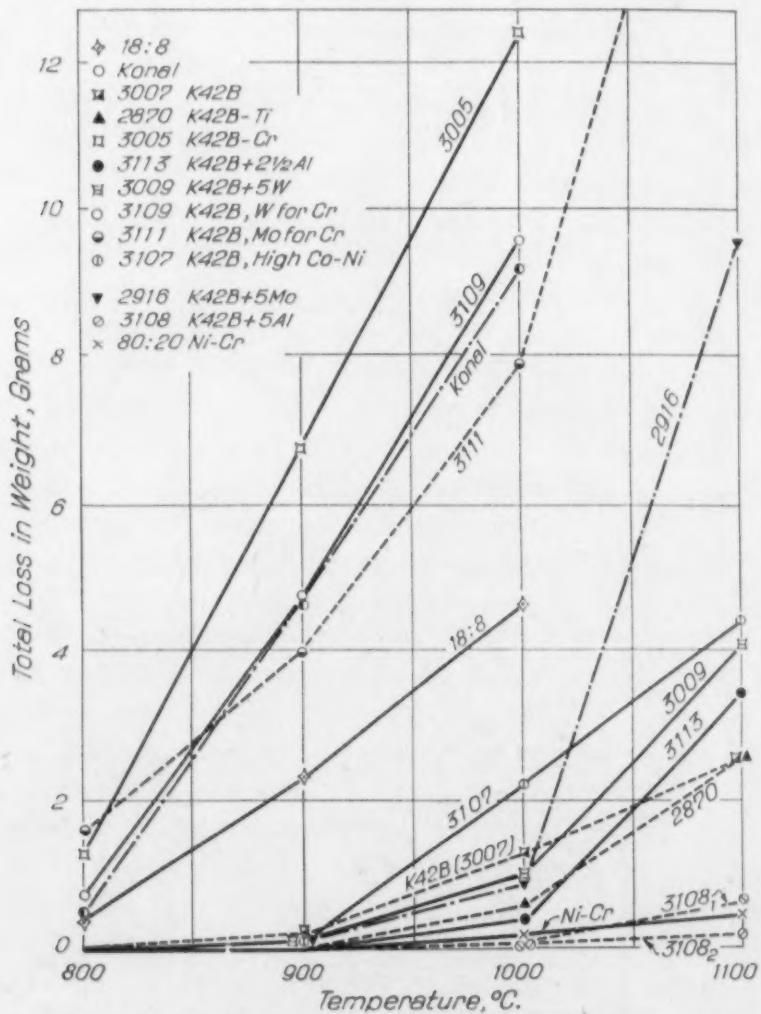


Fig. 14—Effect of Temperature on K42B and Modifications with Stainless 18-8 and Nichrome for Comparison. The Data Indicate Total Loss in Weight After 400 Hours Treatment.

loss was comparable for both specimens (see Table XIV), whereas after 200 hours the weight losses were very different (0.090 grams and 0.509 grams respectively). During the last 200 hours at 1100 degrees Cent., when the "transite" was removed from the furnace, there was relatively little further corrosion of either test sample.

The peculiar behavior of alloy 2916 (Fig. 14) was undoubtedly

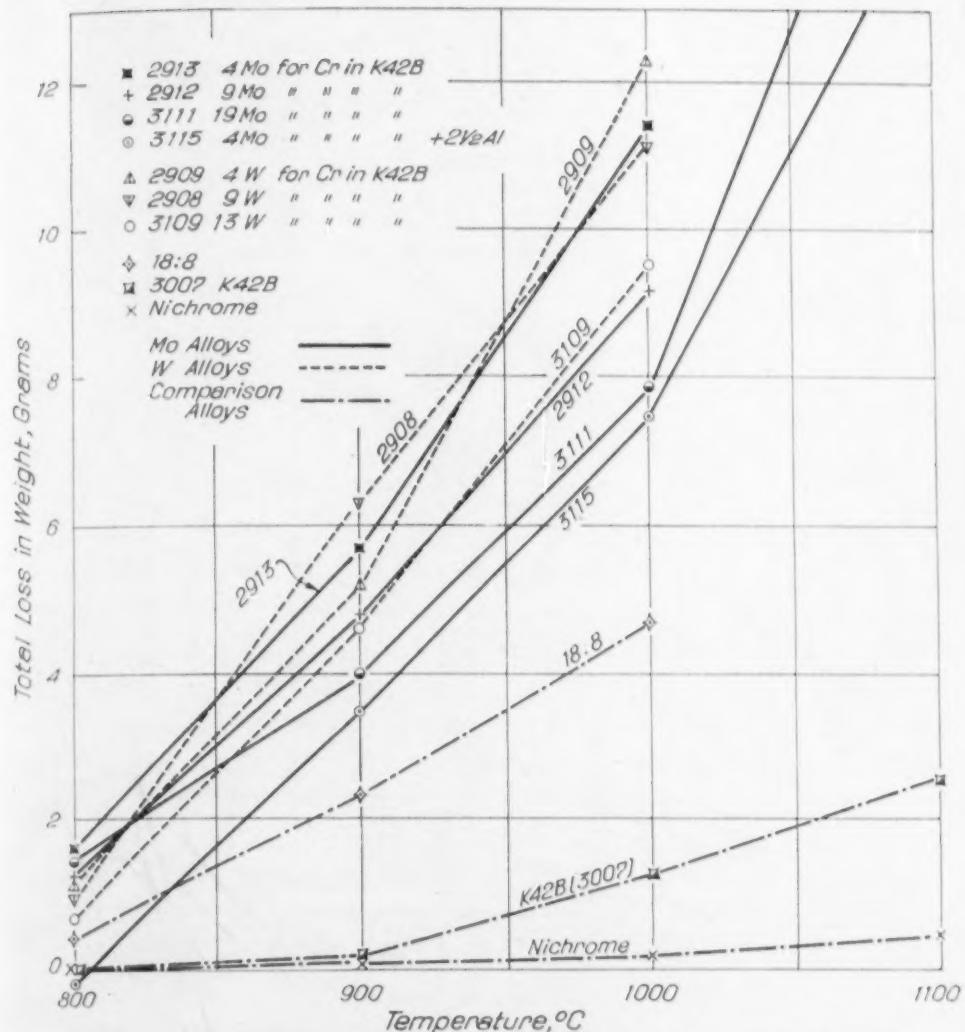


Fig. 15—Comparison of Temperature Effect Between K42B Type Alloys Modified with Molybdenum and with Tungsten. Total Weight Loss After 400 Hours Treatment Recorded.

due to gas attack from the "transite" board. Stainless 18-8 steel is superior to "Konal" but appears markedly inferior to the K42B type alloys.

Fig. 15 illustrates the relative effect of substitution of varying amounts of molybdenum or tungsten for all the chromium in K42B. Both series of alloys are markedly inferior to K42B although increase of alloying elements exhibits definite increase in resistance to scaling. The addition of aluminum (3115) to the 4 per cent molybdenum alloy (2913) shows an important increase in resistance to oxidation.

A general survey of the effect of time and temperature on several modified alloys is represented in Fig. 16. A number of al-

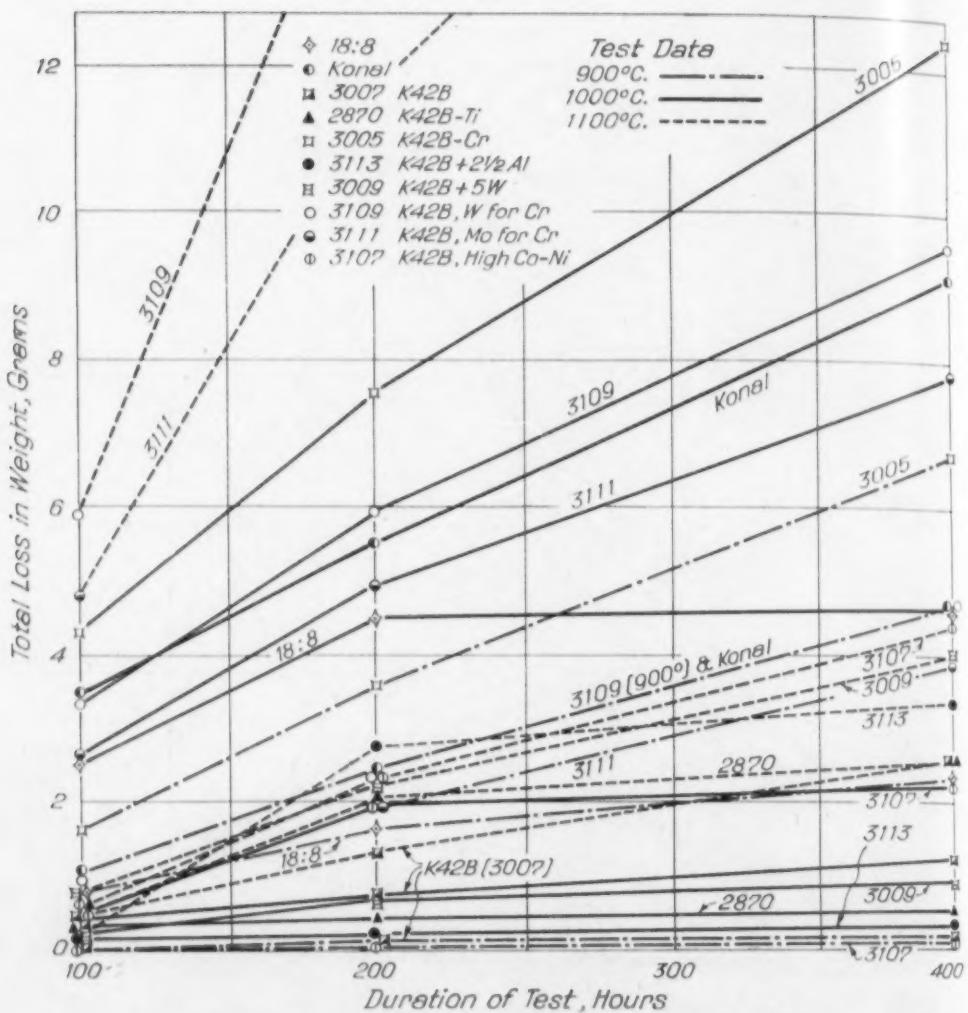


Fig. 16—Effect of Time on Progress of Oxidation of Modified K42B Alloys as Revealed by Total Weight Loss for 100, 200 and 400 Hours Duration of Test. Data for 900, 1000 and 1100 Degrees Cent. are Included.

loys exhibiting high resistance to oxidation are considered in Fig. 17, and the relative progress of oxidation at 800 and at 900 degrees Cent. (1470-1650 degrees Fahr.) is of interest. Alloy 2870 showing the most marked discontinuity with time of test is titanium-free K42B. Aluminum addition (3113) also shows this discontinuity but it is absent in the higher aluminum alloys 3108 and 3114.

#### ELECTRICAL RESISTIVITY

Electrical resistivity is important in certain industrial applications of high temperature materials and a limited amount of data is presented in Table XVI. The specific electrical resistance of iron,

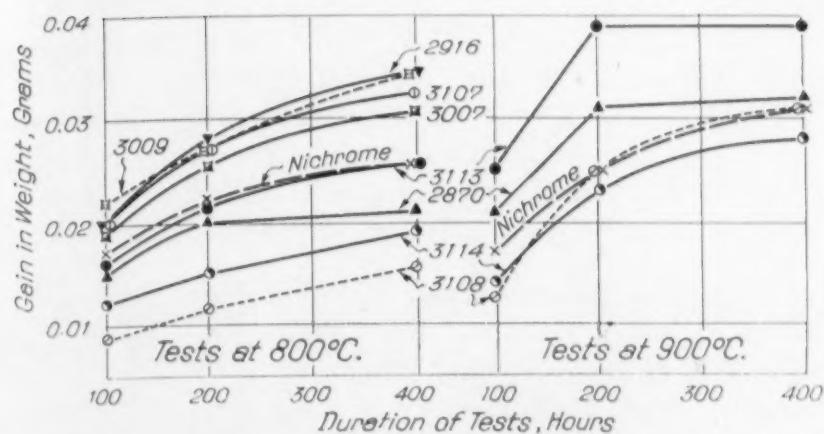


Fig. 17—Comparison of Time and Temperature Effect for Alloys Showing High Resistance to Atmospheric Corrosion.

nickel, cobalt and 80-20 nickel chromium are approximately 10.5, 7, 9.7 and 108 microhms per centimeter cube.

Titanium appears to increase the resistance of the "Konal" type alloys by about 25 units for 2.5 per cent. The introduction of chromium has a marked effect and imparts the major part of the resistivity increase in K42B. Substitution of chromium by tungsten appears to have no effect and molybdenum raises the resistance only slightly.

It is of interest to note the effect of varying the amount of tungsten used to replace the whole of the chromium in K42B. Plotting the data indicates a linear relationship. A near linear relation is also noted between per cent added elements and resistivity when varying amounts of ferrotitanium are added to cobalt.

Table XVI  
Specific Electrical Resistance of Alloys as Quenched from 950 Degrees Cent.

Alloy Designation	Specific Elect. Resist.	Remarks
Konal	44	73 Ni 17 Co 7.5 Fe 2.5 Ti
2866	15.5	Titanium free "Konal"
2867	53	"Konal" with Ni-Co ratio reversed and 4% Ti
K42B	108	46 Ni 25 Co 7.5 Fe 2.5 Ti 19 Cr
2870	95	Titanium free K42B
2907	107	Substituting tungsten for chromium in K42B
2908	68	Substituting 8 tungsten for 19 chromium in K42B
2909	54	Substituting 4 tungsten for 19 chromium in K42B
2910	108	Adding 5 tungsten to K42B
2911	115	Substituting molybdenum for chromium in K42B
2915	82	30 Ni 50 Co 10 Fe 8 Cr 2 Va
2918	100	50 Ni 20 Co 10 Fe 15 Cr 5 W
3006	100	47 Ni 30 Co 7.5 Fe 2.5 Ti 13 Cr
3008	38	15 Ni 40 Co 42.5 Fe 2.5 Ti
3123	62	Cobalt with 20 per cent ferrotitanium
3124	40	Cobalt with 15 per cent ferrotitanium
3125	20	Cobalt with 5 per cent ferrotitanium

## METALLOGRAPHY

All the test samples after the final treatment at 1000 degrees Cent. (1830 degrees Fahr.) were examined under the microscope, and several of the structures observed have been reproduced in Figs. 18 to 22. These photomicrographs represent the structural condition of the alloys after annealing for 400 hours at 1000 degrees

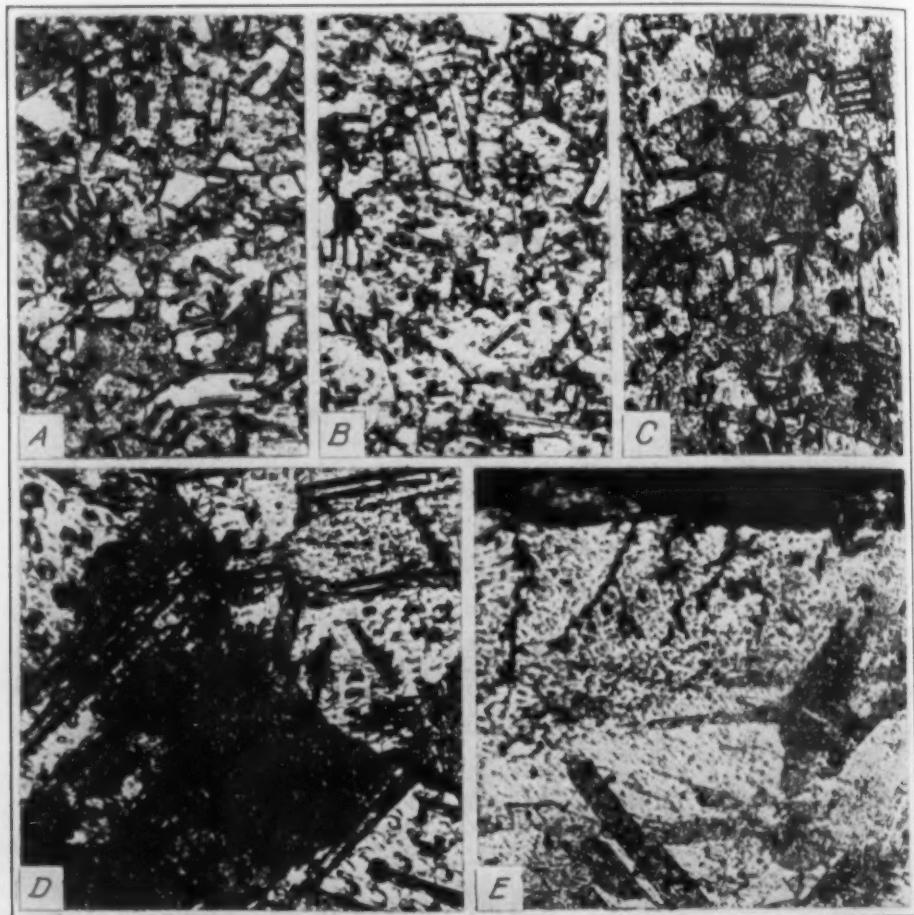


Fig. 18—Photomicrographs of K42B Type Alloys. A. K42B—46 Ni, 25 Co, 10 FeTi, 10 Cr. B. 2870—K42B Without Titanium. C. D, and E. 3107—High Co to Ni Content in K42B—C, Typical Structure; D, Coarse Grain Near Stencil Mark; E, Surface Corrosion. All Photomicrographs Taken After the 400 Hours Oxidation Test at 1000 Degrees Cent. Etched in Nitric-Hydrochloric-Glycerine Solution.  $\times 200$ .

Cent. (1830 degrees Fahr.) followed by furnace cooling. The photomicrographs in Figs. 23 and 24 illustrate forged or annealed structures.

Experimentation with various etching reagents revealed that it was often difficult to prepare a satisfactory clean etch for metal-

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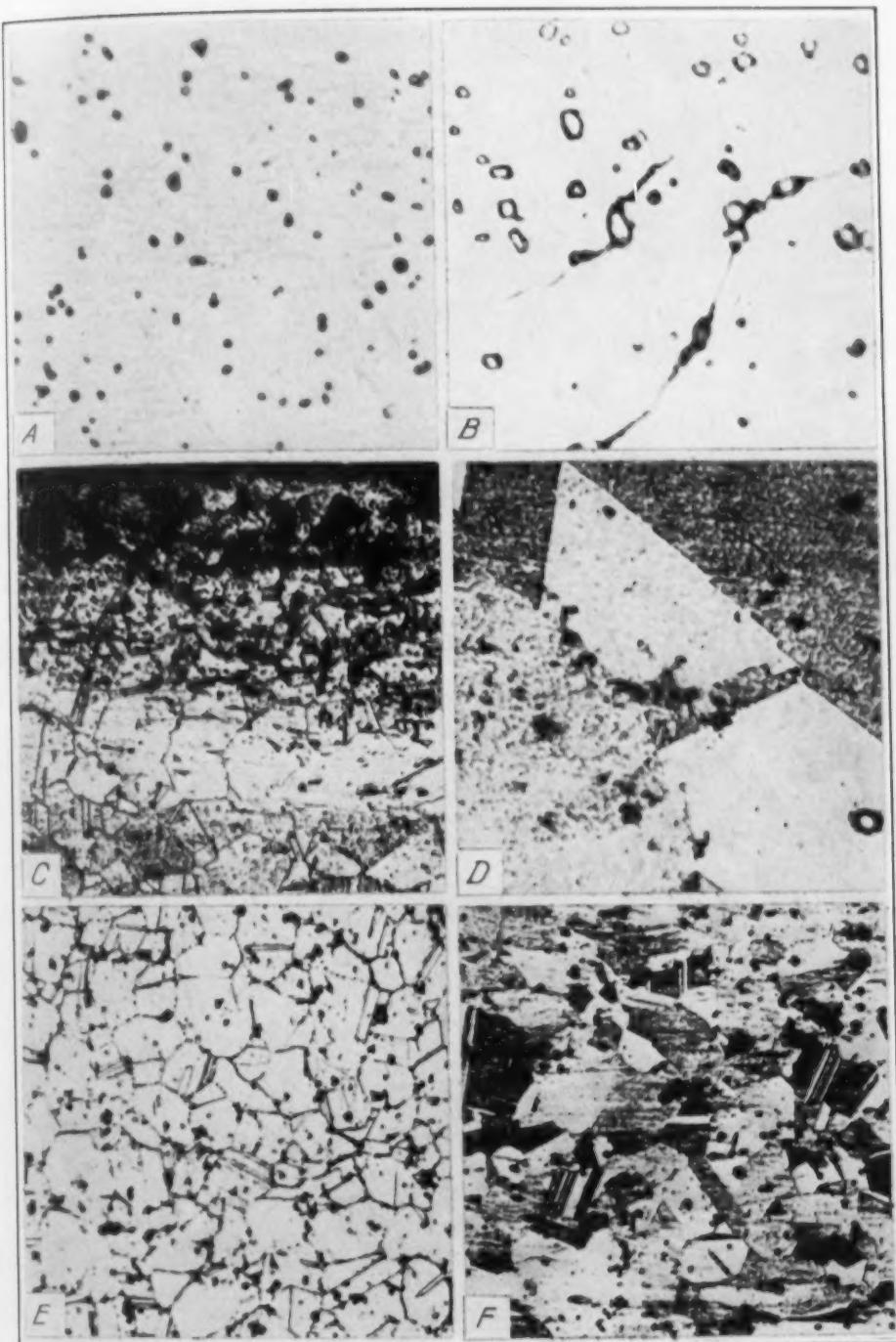


Fig. 19—Photomicrographs of Nickel, Nichrome and K42B with Aluminum. A. Nickel.  $\times 1000$ . B. 80:20 Nickel-Chromium.  $\times 1000$ . C, D, E, and F. 3113—K42B with Aluminum Addition—C, Edge of Specimen.  $\times 200$ . E and F, Typical Structure.  $\times 200$ ; D, Showing Some of the Finer Particles.  $\times 1000$ . Photomicrographs Taken After the 400 Hour Oxidation Test at 1000 Degrees Cent. Etched in Nitric-Hydrochloric-Glycerine Solution.

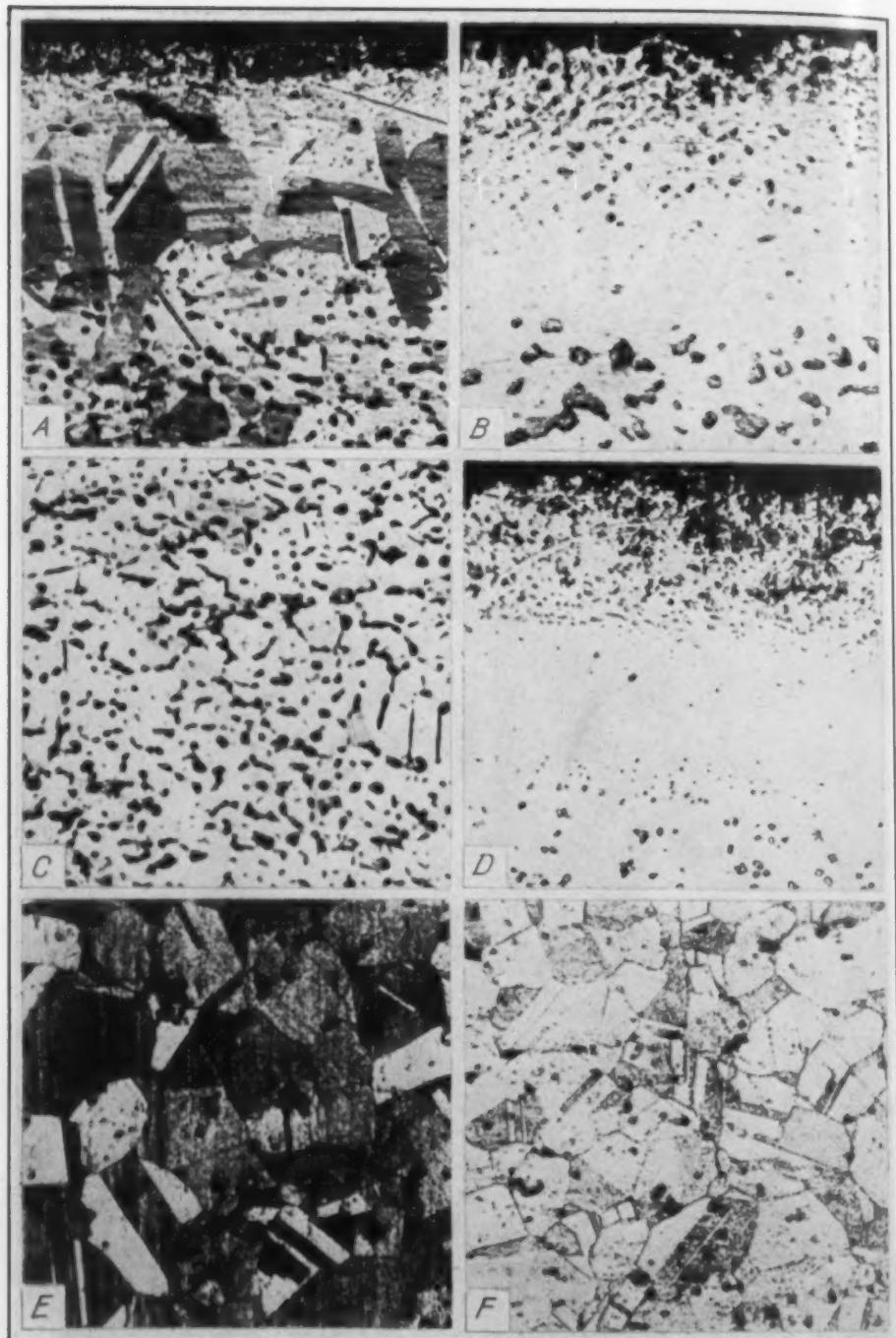


Fig. 20—Photomicrographs of K42B Type Alloys, Containing Aluminum. A and C. 3114—K42B with Aluminum.  $\times 400$ . B. 3108—High Co to Ni Content in K42B with Al.  $\times 200$ . D, E, and F. 3115—4 Per Cent Mo for 19 Per Cent Cr in K42B with Al.  $\times 200$ . All Photomicrographs Taken After the 400 Hour Oxidation Test at 1000 Degrees Cent. Etched in Nitric-Hydrochloric-Glycerine Solution.

lographic examination. Frequently considerable staining and pitting of the alloy occurred. For the oxidation test samples a mixture 1 part nitric, 2 parts hydrochloric and 2 parts glycerine appeared to give the best results.

In Fig. 18 are illustrated K42B, high cobalt to nickel content in K42B and K42B without titanium. These are essentially solid solution type alloys having a fine-grained structure. The coarse structure found in alloy 3107 (D) is taken from a location near where the stencil identification mark was made. This coarse grain was common to many of the alloys and indicated the existence of a critical strain for grain growth. Corrosion penetration may be noted in section E.

Section A and B (Fig. 19) at 1000 diameters illustrates oxygen penetration and phase precipitation in nickel and nickel-chromium alloy respectively. Section C shows oxidation corrosion at the surface, and F shows a typical structure at the center of alloy 3113. Section E resulted from a polish etch attack and is comparable with F. The precipitated particles, presumably due to the presence of aluminum, may be noted. Some of the finer particles are shown at 1000 diameters in section D.

The introduction of a definite phase by further additions of aluminum is readily evident in Fig. 20 where all the alloys contain aluminum additions. Near the edge of the test samples the precipitated phase appears to be oxidized out. Incidentally this phase-free zone tarnished readily. Staining may be due to impoverishment in chromium in the metal immediately under the scale. Again all the alloys are fine-grained, considering the prolonged high temperature treatment. Sections E and F represent the same metallographic structure with two different etching effects.

The addition of 5 per cent tungsten to K42B appears to lead to an increase in corrosion penetration and to an enlarged grain size (A and C Fig. 21). Little account may be given to "depth of penetration" as an evaluation of the susceptibility to corrosion, however, since several corrosion tests of the nature herein discussed showed no penetration by virtue of the rapid scaling which occurred.

The coarse grain in 18-8 stainless steel (Section B) should be noted. Alloy 3111 (19 Mo for 19 Cr) showed a fine grain and a fairly clean structure (E and F). In complex alloys it is difficult to state whether particles disseminate throughout the structure result from nonmetallics introduced during melting, from oxidation

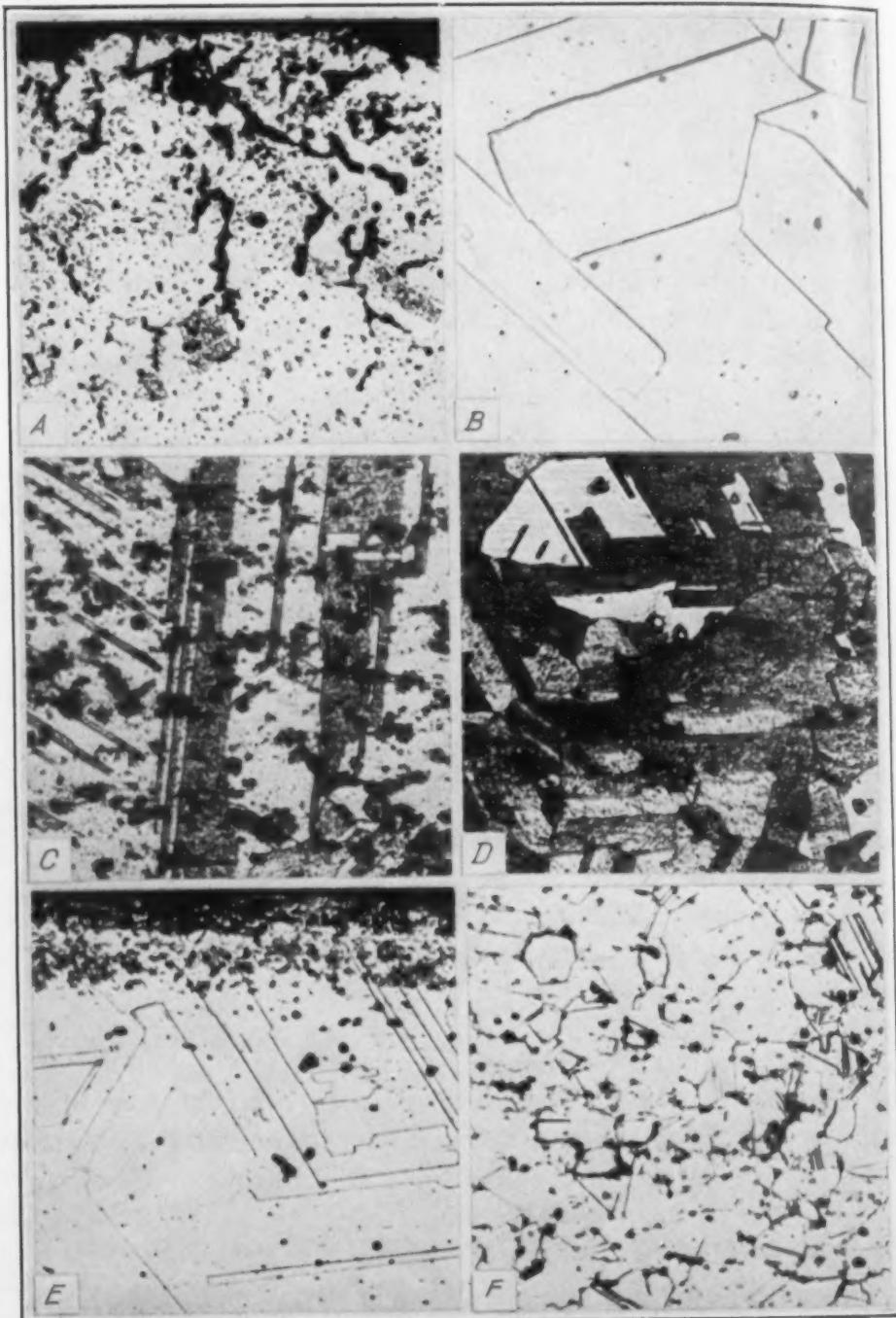


Fig. 21—Photomicrographs of Modified K42B Alloys, Stainless 18-8 Steel and a 2 Per Cent Vanadium Alloy. A and C. 3009—K42B with 5 Per Cent Tungsten Addition.  $\times 200$ . B. Stainless 18-8 Steel.  $\times 200$ . D. 2915—30 Ni, 50 Co, 10 Fe, 8 Cr, 2 Va.  $\times 200$ . E and F. 3111—Mo for Cr in K42B.  $\times 200$ . All Photomicrographs Taken After the 400 Hour Oxidation Test at 1000 Degrees Cent. Etched in Nitric-Hydrochloric-Glycerine Solution.

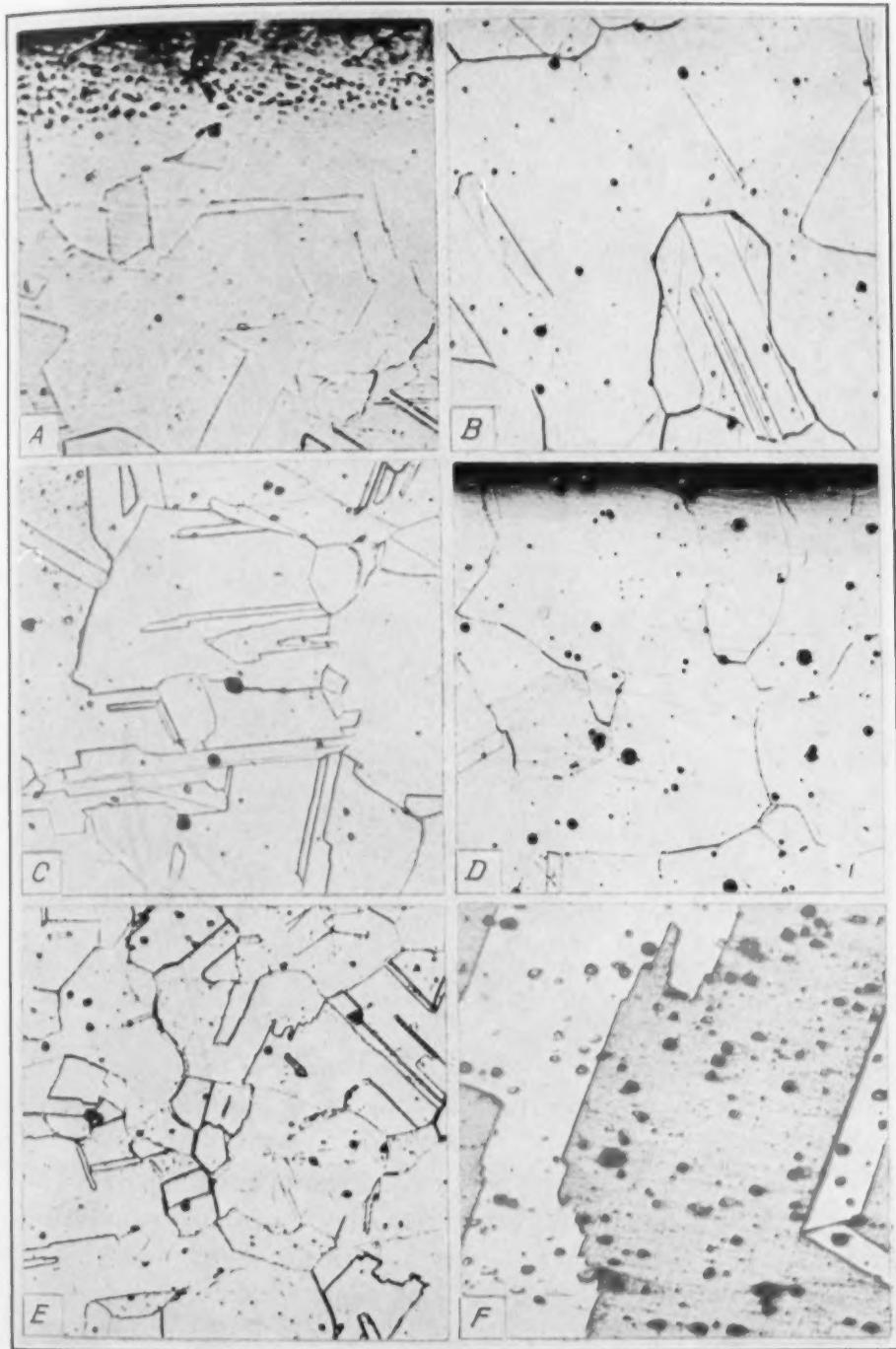


Fig. 22—Photomicrographs of K42B Type Alloys with Molybdenum and Tungsten. A and C. 2912—8 Mo for 19 Cr in K42B.  $\times 200$ . B. 2913—4 Mo for 19 Cr in K42B.  $\times 200$ . D and F. 2908—8 W for 19 Cr in K42B.  $\times 200$ . E. 3109—15 W for 19 Cr in K42B.  $\times 200$ . All Photomicrographs Taken After the 400 Hour Oxidation Test at 1000 Degrees Cent. Etched in Nitric-Hydrochloric-Glycerine Solution.

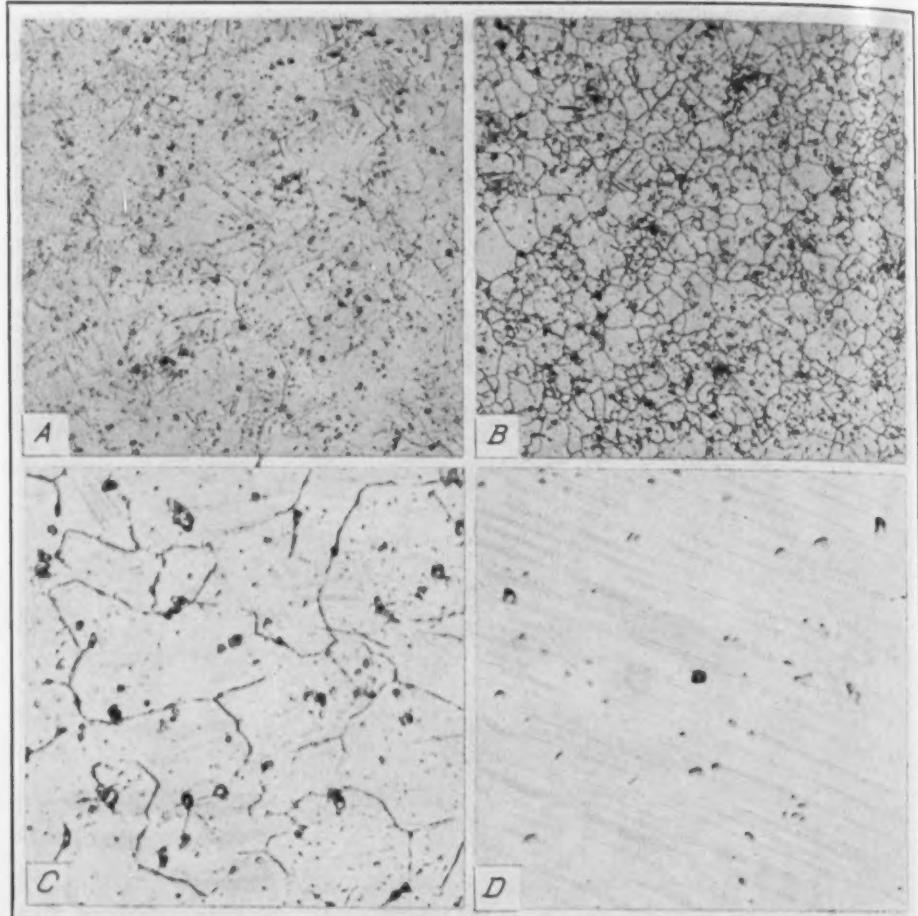


Fig. 23—Photomicrographs of K42B and K42B Type Alloys. A. K42B—As Forged.  $\times 100$ . B. K42B—Quenched from 950 Degrees Cent.  $\times 100$ . C. 2910 (Same as 3009) K42B with 5 Per Cent W. Hot Forged.  $\times 500$ . Etched in Cold Aqua Regia. D. 2912-8 Mo for 19 Cr in K42B. Forged.  $\times 1000$ . All but Section C Etched in Nitric-Hydrochloric-Glycerine Solution.

during the high temperature treatment, or are due to the precipitation of a phase.

Section D (Fig. 22) provides a good example of apparent freedom from intergranular attack and apparent resistance to oxidation corrosion. This 8 per cent tungsten alloy lost weight rapidly in the tests and presumably the scaling kept pace with corrosion attack. Whether the large number of particles is due to heat treatment or is a relic of melting is uncertain.

In Fig. 23 (A and B) is illustrated the forged and annealed sections of K42B. Section C is typical of the hot forged structure of K42B with 5 per cent tungsten addition. The photomicrographs

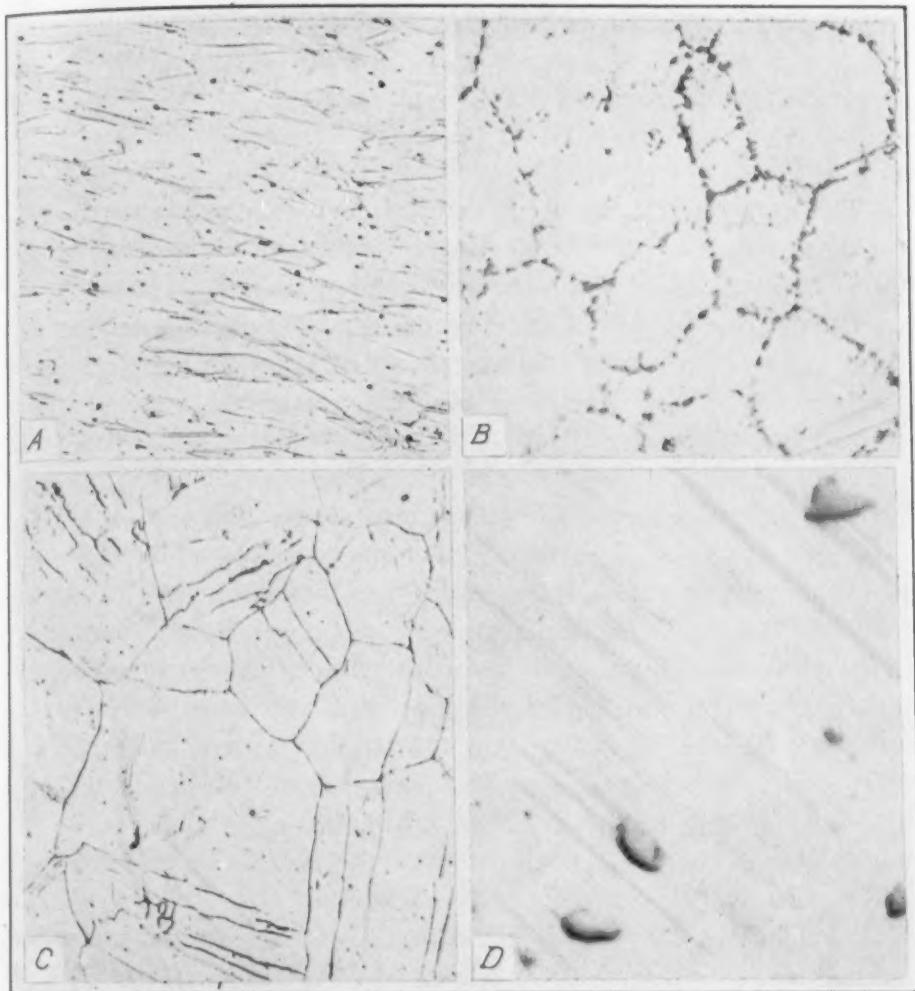


Fig. 24—Photomicrographs of "Konal" Alloys. A. 2866—Titanium-Free "Konal." Swaged.  $\times 100$ . B and D. 2873—"Konal" with 40 Per Cent Fe-Ti. Unetched. B. Annealed at 900 Degrees Cent. and Quenched or Slowly Cooled,  $\times 500$ ; D As Forged,  $\times 1000$ . Note Disperse Phase. C. 2871—75 Ni, 20 Co, 5 Ti. Hot Forged.  $\times 200$ . Sections A and C Etched in Merica's Reagent.

representing this alloy after 400 hours at 1000 degrees Cent. have been discussed (Fig. 21 Sections A and C).

"Konal" with 10 per cent ferrotitanium shows no definite evidence of a precipitated phase, but when 40 per cent ferrotitanium is added a second phase is present in all conditions of heat treatment of the alloy. Sections B and D (Fig. 24) show the appearance of these particles at a magnification of 500 and 1000 diameters respectively. After annealing at 900 degrees Cent. the structure seen in Section B is obtained whether the alloy is slowly cooled or

quenched in water. It is probable that the variation in solubility with temperature of this phase is responsible for the age-hardening characteristics recorded.

#### GENERAL CONSIDERATIONS

The data on resistance to chemical corrosion at room temperature, as revealed by the intermittent immersion tests demonstrate the superior resistance of the alloys to solution in a reducing as compared with an oxidizing acid. The useful duration of a test of this nature is always a matter of conjecture but it is believed that many such tests which have been run for only a few hours may be misleading when used for evaluating corrosion resistance from the practical point of view. The need for extending the test time to several days appears particularly necessary in studying the solution of the alloys in nitric acid, since many exhibit a rapid attack in the early stages followed by practically complete stability due to the formation of an adherent protective film, consisting of the products of corrosion.

In all instances attack by hydrochloric acid appears to be slow but is progressive, and the relatively greater resistance to solution of the three molybdenum alloys is noteworthy. It may be considered that the poor resistance to chemical corrosion of cobalt as compared with nickel is due to the presence of impurities. However, cobalt analyzed 99.32 per cent cobalt whereas the nickel content was only 98.78 per cent.

It would appear that the formation of longitudinal corrosion cracks in many of the alloys is associated with directional properties, and a metallographic study of the corroded test samples should prove informative.

On account of the formation of protective coatings it was also considered desirable to subject the alloys to prolonged oxidation tests at elevated temperatures. During the tests at 800, 900 and 1000 degrees Cent. (1470, 1650, 1830 degrees Fahr.) the maximum change in superficial area due to loss from scaling was less than 10 per cent. Since the data are presented to illustrate important differences in resistance to oxidation, correction for the minor changes in superficial area have been omitted. For a similar reason no attention has been given to the fact that whereas the approximate area of test was 42 sq. cms. for the experiments at 800, 900 and 1000 degrees Cent., by cutting samples for metallographic study, the area was reduced to about 35 square centimeters for the test at 1100 degrees Cent.

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The importance of aluminum additions in decreasing the oxidation due to high temperature corrosion has been established. This agrees with the observations of Zeigler on iron-aluminum alloys.<sup>15</sup> At 800 degrees Cent. (1470 degrees Fahr.) all the best alloys contain chromium; substitution by tungsten or by molybdenum decreases the resistance to oxidation in the order named.

At 900 degrees Cent. (1650 degrees Fahr.) the effect of aluminum and silicon is at once apparent, but despite the addition of aluminum, the alloy containing 4 per cent molybdenum oxidizes rapidly. The alloys containing vanadium are low in resistance even with 8 per cent chromium.

At 1000 degrees Cent. (1830 degrees Fahr.) nickel alone gains weight due apparently to the remarkable tenacity of the oxide coating. The chromium and aluminum alloys do not lose much weight but the silicon does not appear to be so effective. K42B with molybdenum and tungsten additions maintain fair resistance to scaling, but the complete substitution of these elements for chromium makes the alloy scale readily.

The test at 1100 degrees Cent. (2010 degrees Fahr.) is severe and the rate of oxidation is relatively high. Only three alloys, including 80-20 nickel-chromium, scale so little that the loss in weight is of the order of 1 per cent after 400 hours treatment.

Certain characteristics were noted with respect to the nature of the scale formed. At the highest temperature of test all the tungsten alloys and those similar to "Konal" showed a flaky scale which was readily detached. The alloys containing silicon or high content ferrotitanium produced a scale which exploded from the surface during cooling and on standing. Alloys high in iron content exhibited a strong continuous scale which was difficult to remove. It appeared that at least partial fusion of the products of oxidation had occurred. The vanadium alloys also appeared to exhibit definite fusion of the scale.

The high aluminum alloys along with nickel-chromium showed very little surface difference despite loss or gain in weight during test. The majority of the alloys had a discontinuous type of coating which showed a tendency to form tiny cracks over the entire surface.

Metallographic study of the oxidized alloys showed that the

<sup>15</sup>N. A. Zeigler, "Resistance of Iron-Aluminum Alloys to Oxidation," *Transactions, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division*, 1932, Vol. 100, p. 267.

"Konal" and K42B type alloys were essentially solid solutions. In many instances minute particles were observed distributed throughout the structure of an alloy but it was not possible to define these particles as being due to the precipitation of a phase or to the introduction of "nonmetallics" during preparation of the alloys. The addition of aluminum results in the formation of a second phase which can easily be distinguished although not determined.

Most of the alloys exhibit a fine-grained structure even after the 400-hour high temperature treatment, although the formation of coarse grains as the result of critical strain is evident in many alloys.

#### ACKNOWLEDGMENT

The author takes pleasure in acknowledging the co-operation of the Westinghouse Electric and Manufacturing Company in this investigation. He is also indebted to H. D. Nickol, senior student in metallurgy at Pennsylvania State College, for assistance in various ways.

#### DISCUSSION

**Written Discussion:** By George P. Halliwell, director of research, H. Kramer & Co., Chicago.

Dr. Austin's paper, unfortunately, did not come to the writer's attention until a few minutes before its presentation, so that a careful study of it was not permissible at that time. Oral discussion presented by me has been modified and augmented in writing.

The paper is of interest to me not only because of my earlier work on alloys of a composition similar to many used by Dr. Austin, but because of the valuable data on aging and work-hardening. Although a portion of the data on aging was presented in a previous paper,<sup>1</sup> I wish to call particular attention to those alloys which develop high hardness after a suitable thermal treatment. As Dr. Austin has mentioned, "The hardness of aged samples increases with a concomitant increase in cobalt and iron," my natural query arises as to the optimum chemical composition for maximum hardness. If the maximum aged hardness of alloys in the first group, Table I (53-2789) is plotted as contours on a ternary diagram, (nickel, cobalt, iron plus titanium), a clearer picture of the relationship between chemical composition and hardness will be obtained. Whereas the alloys having a high hardness in the quenched condition form a broad plateau in that section of the diagram richer in iron and which rises rather rapidly from the surrounding area, the hardness of the aged samples approaches a peak at about 44 per cent each of cobalt and iron and tapers off gradually toward the iron corner. It is very evident that a nickel-cobalt-iron ratio of approximately 2:7:7 will give maximum hardness upon aging in those

<sup>1</sup>See footnote 1 of Dr. Austin's paper.

alloys containing about 2.5 per cent titanium. This ratio will no doubt change as the titanium is increased or as other elements are introduced. No attempt will be made to hypothecate the cause of such a peak, but I offer this observation as a possibility for further study.

Since many of the alloys listed in the previous paper are known to contain small amounts of carbon, it is possible that the secondary hardnesses noted in some of the alloys shown in Figs. 1 and 2 may be due in part to a precipitation of carbon in some form. Such a double aging effect is well known and would correspond to the precipitation of  $\text{CuAl}_2$  and  $\text{Mg}_2\text{Si}$  in  $\text{Al}-\text{Cu}-\text{Mg}-\text{Si}$  alloys. It is also interesting to note that whereas alloys 2795 and 56 are similar in general chemical composition, they differ considerably in the hardnesses obtained under similar conditions. They vary also in the amount of secondary hardness developed. Alloy 2795 has a total of 1.43 per cent not accounted for in its chemical analysis, whereas No. 56 has only 0.37 per cent. The presence of impurities, silicon or aluminum, introduced with the ferrotitanium, may have repressed this aging, similar to the action of impurities upon the aging characteristic of the binary aluminum-copper alloys.

The influence of other elements upon the age-hardening properties of K42B is very interesting. It is not surprising, however, to find that neither zirconium or tantalum have any beneficial effects on the aging characteristics of this alloy, since early work in the nickel-cobalt-iron base alloys showed that these elements were not interchangeable with titanium in producing marked aging. While the hardness of aged K42B, as modified with molybdenum and tungsten, has been increased within the period of aging, 80 hours, would this improvement be maintained over an extended period? Examination of the available data seems to indicate that it would not. After 1800 hours at 600 degrees Cent. (Fig. 3<sup>(1)</sup>) the hardness is still increasing. At 750 degrees Cent. alloys 2910 and 2916 show definite evidence of softening after 80 hours, whereas K42B (Fig. 5<sup>(1)</sup>), after a slight change due to secondary hardening, has the same hardness after 200 hours as it had at 10 hours. Within the 80-hour limit used in this paper, alloy 2911 is the only one of this group to show a continual increase in age hardness. In other words, has the introduction of molybdenum or tungsten to the K42B composition imparted any real improvement to it in age-hardening over a prolonged period? Finally, none of these alloys has shown the resistance to over-aging shown by K32 (Fig. 3<sup>(1)</sup>), 440 V.H.N. after 3000 hours at 600 degrees Cent. and still increasing.

In comparing the various hardnesses as shown in Tables II and IV and Fig. 5, I should like to call Dr. Austin's attention to certain inconsistencies in the hardness of the "as-quenched" alloys, as noted below.

Hardness of "As-Quenched" Alloys

Alloy	Rockwell C Fig. 5	Equivalent B.H.N.	V.H.N. Table II	V.H.N. Table IV
2869	24+	250	240	260
2916	19.5	228	230	230
2910	19.5	228	250	227
42B	19.5	228	230	225
2918	15.0	205	235	210

The hardnesses as shown in Table IV agree very well with the Brinell Hardness number (Col. 3) corresponding to the Rockwell "C" hardness as given

by the Rockwell Conversion Table, but those of Table II are somewhat out of line. As per Table II, alloy 2910 is slightly harder than No. 2869, yet Fig. 5 shows it to be somewhat softer. A similar condition holds for alloys 2916 and 2918. If the hardnesses given in Table II were converted into Rockwell "C" and taken as the "as-quenched" hardness in Fig. 5, their relative initial position would be changed. I call attention to this inconsistency because Dr. Austin has attributed the increased hardness at 50 per cent cold reduction of 2867 over Konal to its increased cobalt content. If the discrepancies shown to exist between Fig. 5 and Table II apply to other alloys and under varied conditions, it is difficult for the writer to determine the true hardness of these alloys.

The increase in hardness at 50 per cent cold reduction of 2867 over Konal is attributed by Dr. Austin (P. 16, 2nd Paragraph) to the increased cobalt content of the former alloy. This is not strictly true, since 2867 contains 4 per cent titanium. A retarded rate of quench may alone have resulted in a small amount of aging. A comparison of these two alloys with 2866, which has about the same cobalt content as Konal, but no titanium, shows about the same relative differences in hardness in these three alloys, in both the cold-worked quenched and cold-worked aged condition. This would seem to indicate that titanium is the real hardening agent. Further evidence on the relative effects of cobalt and titanium may be seen in the following data.

Alloy	Per Cent				Quenched	Vickers Hardness Number		
	Ni	Co	Fe	Ti		600° C.—50 Hrs.	750° C.—50 Hrs.	Aged
2867	27	54	15	4	150	330	180	
*K32	57	27	10	4.3	210	350	375 Plus	

\*Taken from Table V. Figs. 3 and 5 reference (1).

Although Figs. 5 and 6 show very clearly the relative hardnesses attained by the various alloys, it is the writer's opinion that they do not tell the complete story. It is often desirable to know the proportionate increase in hardness of several alloys. Since K42B has frequently been used in comparison in this paper, I have chosen it as a base, although any other alloy studied could be conveniently used. Starting with the hardness in the "as-quenched" condition and the increase in hardness due to mechanical and thermal treatments as given in Table IV, I have calculated the theoretical proportionate change in hardness of several alloys. The difference between the values obtained (Table IV) and those calculated are designated as plus or minus in the following table.

Alloy	Quenched from 950 Degrees Cent.						
	2869	2910	2916	2868	2867	Konal	
10% Cr	—9	—13	+18	—10	+12	+30	
Annealed to Maximum V.H.N.	—62	+9	+30	+3	+78	+137	
50% Cr	—1	+9	+11	+66	+81	+84	
Annealed to Maximum V.H.N.	+41	+32	+97	+151	+159	+150	
Aged 650 Degrees Cent.—72 Hrs.							
10% Cr	—32	+3	—10	+1	—36	+18	
Aged to Maximum V.H.N.	+14	—5	—3	—6	—15	+6	
50% Cr	—10	—15	—10	—29	—48	+9	
Aged to Maximum V.H.N.	+59	—68	+14	+20	—21	—11	

Examination of this data reveals some striking facts. Alloy 2869 with its reversed nickel-cobalt ratio does not harden upon cold rolling as rapidly as K42B, and only shows its superiority in the aged condition. The addition of

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+81 +84  
+159 +150

—36 +18  
—15 + 6  
—48 + 9  
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5 per cent tungsten (2910) to the K42B alloy, hardens proportionately at a materially slower rate in all conditions, as the amount of cold deformation is increased. The addition of 5 per cent molybdenum (2916) distinctly increases the relative amount of hardening resulting from thermal-mechanical treatment of the "as-quenched" alloy, but has little effect on the preaged samples similarly treated. Alloy 2867 with its high cobalt and titanium presents the most surprising results. While it hardens at a remarkably faster rate in all treatments of the "as-quenched" alloy, the rate is distinctly slower in the preaged state than that of K42B, similarly treated. The lowly "Konal" gives a good account of itself in all but the condition of maximum hardness in the preaged state. I believe that such information gives a clearer picture of the relative resistance of these alloys to deformation.

I must still disagree with Dr. Austin in his statement that too much attention should not be given to the difficulty of forging these alloys. While it is no doubt true that part of the difficulty experienced in the forging operation is due to lack of proper technique in the melting and casting practice, nevertheless that condition exists and until it is improved the alloys will remain difficult to forge. My experience with a large number of these alloys has been that in addition to the presence of any intergranular impurity, most of the alloys are characterized by extreme ingotism, which of itself hinders forging. Once this structure has been broken down and recrystallization effected, further forging is a relatively simple process.

In conclusion, may I express the hope that Dr. Austin will be able to continue this very valuable work, especially in alloys of higher titanium content.

### Oral Discussion

M. A. SCHEIL<sup>2</sup>: I should like to ask Dr. Austin a question in connection with his slide that he showed on the scaling properties of these materials. Of course, these tests which he showed us were continuous scaling tests and I would like to know if he has made any attempts at accelerated scaling tests such as in and out tests, in which the scale was given a chance to break off the specimen.

We have done some work of this kind on different alloys and we have noted that loss in weight from continuous scaling tests is not always a good indication of the scale resisting properties of an alloy in connection with a study of this kind. For instance, we might have internal oxidation or grain boundary oxidation which would give a mistaken idea of the ability of the alloy to resist oxidation.

### Author's Closure

I welcome the discussion of the paper by Mr. Halliwell and much appreciate the effort he has put into his analysis of the work presented in Part I.

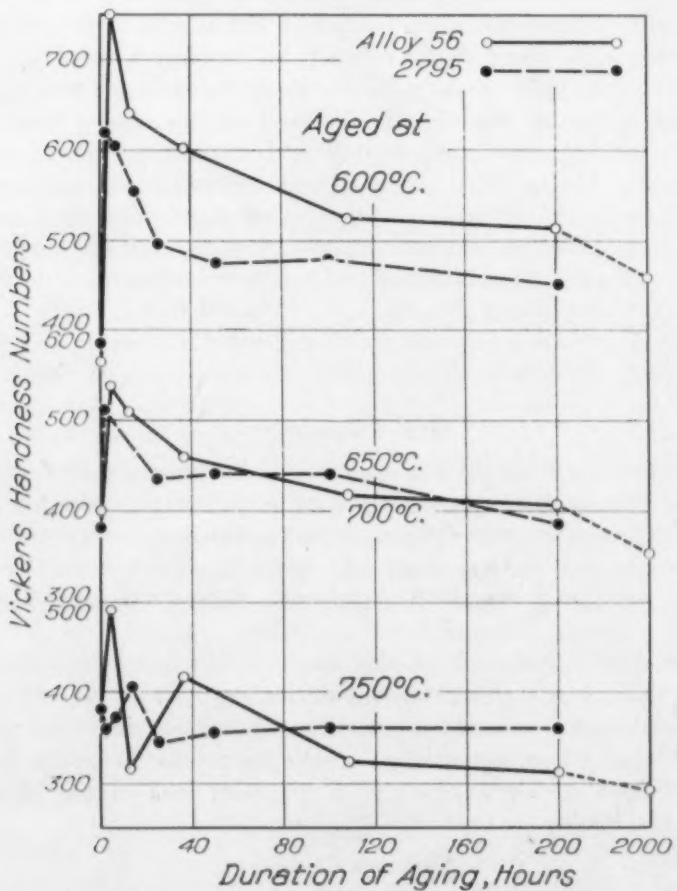
It is common practice to attempt to evaluate physical properties of a ternary system in terms of its three components in a manner similar to that used in studying alloy constitution. We have tried to do this, using a three dimensional triangular model, in an effort to correlate tensile strength and elongation per cent with the composition of the alloy. From such a model it

<sup>2</sup>A. O. Smith Corp., Milwaukee.

was evident that cobalt was more powerful than nickel in raising the tensile strength.

An analysis of this kind is most simple when considering the alloys in the quenched state. Since, however, the most interesting properties are obtained after some aging treatment, and since the true picture would be obtained only after subjecting each alloy to the heat treatment yielding optimum properties, it seems that little is gained by the above considerations until more knowledge is available on the constitution of the alloys.

Mr. Halliwell suggests that the secondary hardening observed in Figs. 1 and 2 may be due to carbon, and draws attention to two alloys (2795 and 56) which have similar chemical composition. In order to obtain a clear picture



of the relative behavior of these two alloys the data on aging have been presented in the accompanying figure. There is a marked difference in behavior although the general trend of reaction to aging is similar. Alloy 2795 is softer than 56, aged at 600 degrees Cent., but harder when aged at 750 degrees Cent. It is interesting to note that heat treating alloy 56 at 700 degrees Cent. gives very similar data to those obtained by heat treating alloy 2795 at 650 degrees Cent.

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Attention is drawn to the discrepancy in total per cent from chemical analyses. The author has no means of checking back on this discrepancy but he happens to have available chemical analyses for minor elements in these two alloys.

	Aluminum	Manganese	Silicon	Carbon
Alloy 56	0.31	0.11	0.33	0.07
Alloy 2795	0.24	0.38	0.47	0.11

It would seem that the difference in aluminum and silicon content cannot have materially assisted in contributing to the difference in aging characteristics of the alloys, and the carbon content is lower (0.07 per cent) in the alloy (56) which exhibits the greater secondary hardening. Nevertheless, there is ample evidence to show that carbon may have an important effect on the hardness of the alloys.

The author's reference to substitutions for titanium as hardening elements referred more particularly to zirconium, vanadium and silicon, and he would like to draw Mr. Halliwell's attention to the fact that early work did not show that zirconium and tantalum could not be interchanged with titanium. In our joint earlier paper it appeared that the substitution of either of these two elements for titanium did not lead to age-hardening "pure nickel" alloys (See Alloys 15 and 19, page 8 Ref. 1), but neither does titanium, (Table II, Konal II) even in the presence of iron—and it is believed that the iron-titanium compound Fe<sub>3</sub>Ti is responsible for the high temperature hardening in most of the alloys studied.

Reference is next made to the effect of additions of tungsten and molybdenum to K42B. To the author there appears to be a marked difference in behavior of alloys 2910, 2916, and 2911 (alloys cited by Mr. Halliwell) compared with our earlier basic alloy K42B, when aged at 600 degrees Cent. (Fig. 3). It must be remembered, however, that so high a temperature as 750 degrees Cent. tends to reduce or destroy any marked difference in hardness. It should be of interest to compare other properties of these alloys by reference to Part II of this work.

Alloy K32 is a remarkable alloy when considered in the light of its resistance to over-aging at 600 and at 650 degrees Cent. This alloy, however, contains about 4.5 per cent titanium and it is not strictly comparable to the standard 2.5 per cent titanium alloys. This comment is also true of "Super Konal"—Alloy 2873 (Fig. 4). It may be noted that when heat treated at 750 degrees Cent. K32 is definitely inferior to K42B as regards its resistance to over-aging.

Mr. Halliwell next cites certain inconsistencies in hardness values recorded in Tables II and IV. If reference is made to the initial paper on this system of alloys it may be noted that the basic alloy "Konal" cannot be regarded as having a definite quenched hardness. Thus in Figs. 3 and 4 of that paper it is shown that the quenched hardness for the "Konal" specimen aged at 600 degrees Cent. was about 140 whereas the quenched hardness of the specimen used for aging at 650 degrees Cent. was about 165 V.H.N. Both these values were obtained by actual test on a Vickers machine so that the difference is not due to translation to an "equivalent" hardness number in another system. Dif-

ference in quenched hardness of two specimens of the same alloy (56) can be observed in the accompanying figure. The values range from 370 to 400 V.P.N.

In the study of complex systems of alloys such as those discussed in the present paper it is impossible to obtain exact agreement in hardness values. Slight segregation in the small experimental ingots may contribute to this variation, and phase precipitation during grinding of the quenched specimen may occur due to accidental over heating. Thus the slight variation in quenched hardness of 2910 and 2869 is not significant, but it is believed that the difference in reaction to cold work (Fig. 5) is real.

The author agrees that it is difficult to apportion the credit for increased hardness of alloy 2817 since both cobalt and titanium are present in greater quantity than in "Konal." In systems of more than two components it is not possible to be sure of the exact role of any element unless data on the constitution of the alloys are available.

The author considers that the data on K32 and 2867 which Mr. Halliwell uses as further evidence of the effectiveness of titanium as a hardener might with more justification be used to demonstrate how important is the role of nickel as a hardening element. The author was surprised and at a loss to explain the poor reaction to aging of alloy 2867 at 750 degrees Cent.

It took considerable study to elucidate how Mr. Halliwell had arrived at the data shown in his list of derived values with the positive and negative values, and the author feels that the picture Mr. Halliwell brings out may be observed qualitatively from the general change in slope of the curves in Figs. 5 and 6 and in Fig. 7. The relative change in hardness had been considered but it was thought that the absolute values at any treatment were more important. Many methods of analysis of the data may be used and for this reason the author presented the data as fully as possible.

As regards forging difficulties the author believes that Mr. Halliwell finally suggests that such difficulties are only temporary. Perhaps, however, stress should be given to the idea that a study of precasting treatment and of casting technique would materially assist in the initial breakdown of the ingot.

The author is glad to have Mr. Scheil's comments on scaling. The method adopted to examine the resistance to oxidation of the alloys is explained in Part II of the paper, and consisted of three periods of heating at constant temperature for 100, 200, and a total of 400 hours. Cooling and shaking of the samples in between these heats would partially simulate what Mr. Scheil mentions. Probably the most satisfactory test for what he has in mind is the standard A.S.T.M. test for electrical heating wires.

It is true that the weight loss data alone does not give information on penetration or on structural change. The author attempted to supplement this work with a metallographic study of the alloys after the final treatment. Since Part II of the paper was not preprinted it was not possible to give adequate attention to a discussion of this phase of the work.

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## X-RAY METHODS FOR TERNARY SYSTEMS

By A. G. H. ANDERSEN AND ERIC R. JETTE

### Abstract

*While the fundamental principles which are applied in studying the constitutions of ternary systems by X-ray methods are the same as for the binary systems, ternary systems involve a number of complexities which must be understood if investigations of such systems are to be performed efficiently. In particular, the methods of interpolation and extrapolation of lattice constant measurements as functions of composition differ in important ways from those used in binary systems. In this article the authors discuss the underlying theory of the use of X-ray methods for studying ternary systems and describe the methods which they have already employed in their recently published investigation of the iron-chromium-silicon phase diagram.*

### INTRODUCTION

THE application of the methods of crystal structure analysis by X-rays to the study of the constitutional diagrams of binary alloys is now well established and has resulted in a considerable body of useful information. The application to ternary systems has not yet received much attention and to our knowledge no record of an extensive investigation of a ternary system has appeared. Both practical and theoretical interest in alloys with more than two components are constantly increasing. In the hope that X-ray studies of such systems would prove to be as fruitful as those in binary systems, such studies have been inaugurated in this laboratory.

The general principles which are to be applied in X-ray studies of the more complex systems are, of course, fundamentally the same as those which have been used in binary systems. The methods of applying these principles to the more complex systems differ in important details.

In order that we should be able (1) to restrict the amount of

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Of the authors, A. G. H. Andersen is with the Phelps Dodge Corporation, Research Department, and Eric R. Jette is Associate Professor of Metallurgy, School of Mines, Columbia University, New York City. Manuscript received February 14, 1936.

exploratory work, (2)<sup>1</sup> to use the X-ray methods to their fullest advantage, and (3) to make the actual procedure as systematic as possible, we found it not merely convenient, but actually necessary to inquire into the general conditions governing the application of X-ray techniques to ternary systems by deductions from the known facts of the pertinent sciences. Since the results of this investigation are of such a general character that they are not limited to any particular ternary system and really constitute a basis for X-ray investigations of ternary alloys, they are communicated separately in the present article.

Regarded from the viewpoint of physical chemistry, a metal system is a series of heterogeneous equilibria, and the determination of the constitutional diagram of such a system is essentially an application of the phase-rule to a number of fairly well standardized measurements of characteristic properties of metals. Before beginning a work of this nature, it is therefore desirable to define a few of the terms which are to be used, which otherwise, perhaps, might be the cause of confusion.

All such terms as component, phase and equilibrium are used strictly in the phase rule sense. However, it is becoming customary with metallurgists, in dealing with metal systems, to use the term "equilibrium diagram" with some caution, on account of the uncertainty of attainment of equilibrium at lower temperatures where, though the free energy changes may be large, the reaction rates may be extremely slow. The long predicted and recently demonstrated instability of cementite in hypoeutectoid steel is a point at hand (1).

A better term for use in metal systems is constitutional diagram or phase diagram, with the understanding that the approach to true equilibrium is as close as practical conditions permit. The crucial test for equilibrium is often considered to be an approach towards the equilibrium from two opposite directions, and observation of any divergence in the results obtained. This method has its obvious limitations for use with metal systems when a low temperature equilibrium is to be established. There seems to be a distinct correlation between the decrease in reaction or diffusion rates in solids and the increase in rigidity of the solid. The rigidity, as is well known, increases as the temperature decreases. If a divergence is observed within any practically available treatment time, one may conclude that equilibrium was not obtained with both approaches.

<sup>1</sup>The figures appearing in parentheses refer to the bibliography appended to this paper.

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In many cases, the only way of insuring a close approach to equilibrium would be to hold the materials at a specified temperature for months and even years, and this has occasionally been done in some types of investigations. In most cases, even when desirable, such a procedure is out of the question and some sort of compromise is adopted, such as treating selected alloys for various lengths of time at identical temperatures and comparing the results obtained with different times of treatment on each alloy.

Where the term intermetallic compound is used, it is with reservations that such a substance may be capable of dissolving one or more of its constituents to a certain extent. The term "secondary solid solution" proposed by Hume-Rothery is frequently used in this connection. In ternary systems, solid solutions of this type would be called "secondary ternary solid solutions," which is not only confusing but cumbersome. True compounds satisfying the criteria of definite proportion and invariant composition are comparatively rare in metal systems.

#### TEMPERATURE-COMPOSITION RELATIONSHIP IN TWO-PHASE EQUILIBRIA

In any system of two or more components we may consider that, in general, every phase is to a greater or lesser degree variable in composition. It is true that in some cases the range of composition is so small that we may for convenience refer to them as pure elements or as compounds. Thus, in general, every two-phase region in a ternary system may be discussed as the equilibrium between two conjugate solutions. Again, in general, the compositions of two such phases in equilibrium will vary more or less with the temperature, and, in ternary and more complex systems, with the gross composition of the alloy as well. Thus the case of an intermetallic compound in equilibrium with another phase may be treated in essentially the same way as conjugate solutions.

The relationships existing between alloy composition and composition of phases in equilibrium will be mathematically demonstrated below for a two-phase region in a ternary system. A co-ordinate system indicating temperature and three constituent compositions is employed.

Starting with an alloy of a predetermined composition, the compositions of the phases under conditions of equilibrium may be expressed as functions of temperature. Referring to Fig. 1, let the

components be A, B, and C, and let the composition of the alloy be, a% of A, b% of B and c% of C. The composition of one of the phases in the equilibrium, for instance an intermetallic compound of variable composition, may then be expressed as h% of A, k% of B and l% of C, when h, k and l are functions of temperature; the

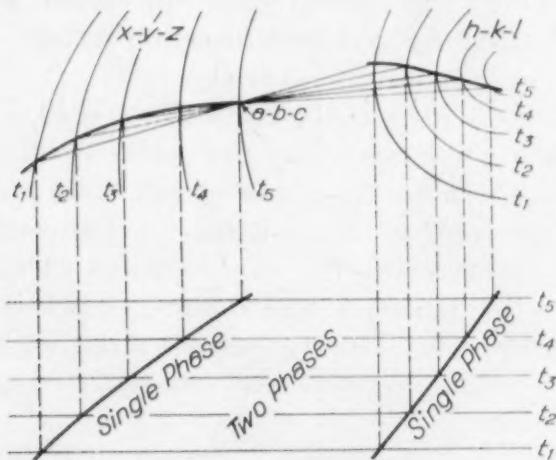


Fig. 1—Distribution of Constituents as Function of Temperature; Three-component, Two-phase Equilibrium.

composition of the remaining phase may then be expressed as x% of A, y% of B and z% of C, and it may be determined as follows:

Starting with 100 grams of alloy, after u grams of compound has been formed, we have  $(a - uh/100)$  grams of A,  $(b - uk/100)$  grams of B and  $(c - ul/100)$  grams of C left in the other phase, and its composition in percentages is:

$$\begin{aligned} x &= 100 (a - uh/100) \div (100 - u) = (100a - uh) / (100 - u) \\ y &= 100 (b - uk/100) \div (100 - u) = (100b - uk) / (100 - u) \\ z &= 100 (c - ul/100) \div (100 - u) = (100c - ul) / (100 - u) \end{aligned}$$

Under equilibrium conditions, u is a function of temperature; h, k and l are likewise functions of temperature and cannot vary independent of u; they are therefore also functions of u. However, at any fixed temperature within the range at which the process may take place, h, k, and l are functions depending only upon the composition of the alloy under consideration; therefore, h, k and l have quite definite values at any such chosen temperature; and if under such a condition u should be considered variable we are obviously no longer dealing with equilibrium. This condition, if u increases, results in a familiar type of reaction which is of considerable prac-

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tical interest since it is the process which occurs in precipitation hardening phenomena where, as is well known, precipitation takes place out of a supersaturated solid solution during annealing at a suitable temperature. Differentiating these equations with respect to  $u$ , we get:

$$\frac{d(x)}{d(u)} = \left[ (100 - u) \left( -h - u \times \frac{d(h)}{d(u)} \right) + (100a - uh) \right] \div (100 - u)^2$$

$$d(x) = [100(a - h) \cdot d(u) - (100 - u) \cdot u \cdot d(h)] \div (100 - u)^2$$

$$d(y) = [100(b - k) \cdot d(u) - (100 - u) \cdot u \cdot d(k)] \div (100 - u)^2$$

$$d(z) = [100(c - l) \cdot d(u) - (100 - u) \cdot u \cdot d(l)] \div (100 - u)^2$$

And:

$$\frac{d(x)}{d(y)} = \frac{100(a - h) \cdot d(u) - (100 - u) \cdot u \cdot d(h)}{100(b - k) \cdot d(u) - (100 - u) \cdot u \cdot d(k)}$$

and similarly for the other ratios.

Recalling that  $u$ ,  $h$ ,  $k$  and  $l$  are functions of temperature, it is seen that this equation describes the variation in composition of two phases in equilibrium.

At constant temperature the equation may be considered to hold for the precipitation process though the system is no longer in equilibrium. For the sake of simplification we shall assume that the composition of the precipitating phase has during the course of the precipitation the same composition  $h$ ,  $k$ ,  $l$  as at equilibrium. The above expression then reduces to:

$$\frac{d(x)}{d(y)} = \frac{a - h}{b - k}$$

since  $d(h)$  and  $d(k)$  are zero, and this special form would, of course, have been obtained directly by partial differentiation.

Integrating the latter equation, we get:

$$x = \frac{a - h}{b - k} \cdot y + C \text{ which is a straight line formula, and describes a tie-line.}$$

The limiting values of  $x$  and  $y$  are set by the attainment of equilibrium and are therefore given by the original equations for  $x$  and  $y$ . When these limiting values are substituted in the integrated equation, we obtain:

$$C = a - \frac{a - h}{b - k} \cdot b$$

Substituting this value of  $C$  in the integrated equation, we obtain:

$$x = \frac{a - h}{b - k} (y - b) + a \quad \text{or,} \quad \frac{x - a}{y - b} = \frac{a - h}{b - k} = \frac{x - h}{y - k}$$

as the equation for a tie-line.<sup>2</sup>

The changes in composition of the two phases of a given alloy with temperature are thus, under equilibrium conditions, represented by space-curves on a ruled surface which pivots on the point indicating the alloy composition. (See Fig. 1). These space curves represent the intersection between the pivoting ruled surface and the solubility surfaces. Temperature sections of this pivoting ruled surface are identical with tie-lines and describe the path along which a metastable or suspended equilibrium must tend to adjust itself at any given temperature. These space curves can easily be represented by projections with a temperature section as a base plane as shown in Fig. 1, and may be of some interest for future studies of the thermodynamics of reactions in metal systems.

#### METHODS AND GENERAL PRINCIPLES

The characteristic properties of each phase present in a system are in general, at constant temperature, continuous functions of its composition whether present in a single-phase field or in a mixed-phase field. While in a single-phase field, the composition of the primary phase is, naturally, identical with that of the alloy, this can, of course, never be the case in a two-phase field. A function, therefore, which gives the relation between the alloy composition and such a characteristic property as lattice-parameter of a phase present in two adjoining phase fields, must suffer a discontinuity at the phase boundary line. The criterion must be used with some caution, however; as has been demonstrated for the binaries of iron with chromium and with silicon, even within single phase regions, sudden changes of direction may appear which resemble discontinuities. Close examination of the experimental facts and their co-relation to theoretical possibilities of atomic arrangements, such as has been demonstrated by Jette and Greiner (2), makes it evident that the discontinuities may be only apparent, and possibly may constitute nothing more than rapidly changing portions of continuous functions.

<sup>2</sup>Although this derivation for the tie-line equation in a ternary system is certainly not generally known, it may not be new. Our search in a few portions of the voluminous literature on phase rule where it could be expected to be found, failed to reveal it.

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The appearance of a new phase cannot, therefore, with certainty be inferred from such a discontinuity alone; the possibility of its existence from a phase-rule standpoint should be investigated and direct or strong corroborative evidence of its presence should be sought. However, once the presence of a new phase has been established, the limits of its range may be determined from observance of discontinuities of the functions.

Identification of phases may be satisfactorily carried out by means of powder photographs, regardless of the fact that complete determination of crystal structure can rarely be made without resort to the Laue-methods or the rotation-technique, except when the structures to be determined are of the simpler types. The difficulties encountered in preparation of single crystals, necessary for these latter methods, restrict their use, practically, to investigations whose essential object is the determination of crystal structures.

Determination of solubility limits may be carried out by means of powder photographs by simple identification of phases without measurements of lattice parameters; employed in this fashion, the method is distinguished from the classical microscopic technique not only by the substitution of X-ray apparatus for microscopic equipment, but also in the manner of heat treatment and preparation of samples. The vacuum-treatment, the smaller bulk of the samples, and the high quenching speed which these make possible are inherent advantages in the powder method and frequently offer advantages over the more massive samples necessary for the examination of polished sections. These advantages, however, are to some extent lost by use of the method for a simple recognition of phases, due to the fact that a considerable proportion, probably several per cent, of the secondary phases must be present in the samples before their presence will be shown by lines on the photographs.

Full benefit of these advantages may, however, be obtained by measurements of the lattice parameters. Differences in the limiting composition of the phases amounting in some systems to a few hundredths of a per cent may be recognized by means of the photographs. For ternary systems, however, no such high accuracy in the determination of solubility limits is generally attainable. This is due to the fact that the magnitude of the variations in lattice parameters with temperature in ternary systems is dependent upon the composition of the alloys, the slope of the parametric surface and the direction of the tie-lines. Even where possible, the attainment of an ac-

curacy of say 0.1 per cent on the boundary curves would require an inordinately large number of alloys.

The ideal way of utilizing lattice parameters for establishing solubility limits would involve the measurements of the parameters at the actual temperatures employed without quenching, a procedure which would be comparable to that of obtaining expansion rates with a dilatometer. No adequate technique of general utility for this purpose is yet in existence for temperatures as high as required for work on many important alloy systems.

In determining the solubility limits by means of the X-ray technique, it is assumed that discontinuities observed in the lattice constant versus composition curves in binary systems or surfaces in ternary systems at room temperature, occur at the same composition as at the quenching temperature. A phase of a given composition has the same coefficient of thermal expansion at various temperatures whether it is by itself or forms part of a two or polyphase alloy. For this reason the expansion or contraction involved in the temperature change ordinarily does not affect the location of the solubility limit. It occasionally happens, however, that the composition of the phase under consideration lies beyond the limit where its lattice constant can be measured for single phase alloys. In ternary systems, there is an additional factor in that the composition of this phase usually does not remain constant in the neighboring two-phase area. In both cases extrapolation of lattice constant versus composition curves or surfaces must be made. Because of the method of obtaining the intersections, it is still possible to have an error in the solubility determination when quenched specimens are used. The functions giving the relation between lattice parameters and compositions are known with a precision which depends upon interpolation between individually determined parameters and not only the absolute value of these changes must be considered but also their value relative to each other. Interpolation from points obtained by measurement at room temperature may therefore give a slightly different intersection point from one that could be obtained at the actual temperature level of the equilibrium. The precision obtainable in either case will also depend upon the angle of intersection of the representative curves which may differ at different temperatures. By obtaining alloys close to the solubility limit, however, the correct value will be approached with nearly equal certainty by measurements at high and at low temperatures. There is not enough known about the thermal expansion

coefficients for us to determine how important this restriction may be.

Even after major changes of composition due to precipitation, solution, etc., have been eliminated by the use of sufficiently high quenching speed, there is still a very important assumption made in X-ray work of this type. This assumption is that during the quenching operation itself nothing has taken place which would cause a change in the lattice constant other than that due to the pure contraction phenomenon. This assumption is not generally valid. Even under the best obtainable conditions, a certain amount of reaction (precipitation or solution) is apt to take place. The strains produced by such reactions are considered together with other strains under the general term "quenching strains."

Such strains must be of a complicated nature and consist not only of ordinary heat-contractive strains in a continuous phase, but also of interfacial tensions, strains due to the difference of the expansion coefficients of two intimately mixed phases and possibly other sources including the reactions mentioned above. As a rule, formation of an intermetallic compound involves a volume change. The volume of a compound is generally less than the sum of the volumes of the constituent atoms, but the reverse is occasionally true. In most cases the specific volume of the supersaturated solid solution increases with decreased concentration of a secondary metal. The net result may be radial tensile stresses and, more rarely, compressive stresses in the compound and in the abutting solid solution. The intensity of these stresses must be of a much greater magnitude in the compound than in the larger volume of its abutting matrix. The lattice of the compound under conditions of tensile stresses must be under strains the intensity of which increase from the interface inward toward the center of the incipient compound particle. The interference lines from such a constituent should be expected to register as more or less hazy and broad lines on the photographs. If a considerable number of particles were present at the quenching temperature, this condition might be intensified or diminished according to the difference in heat expansion rates of the constituent phases. Distortion of the reflections which may possibly have been caused in this way have been discussed by many investigators, e.g., see (3).

An investigation of the effect of quenching strains on the lattice parameters of aluminum-copper alloys was made by Phillips and Brick (4) using a back reflecting camera and wires and powders of varying diameters. The authors found that quenching strains did

not affect the size of the parameters of solid solutions when the diameter of the material was less than 0.125 inch; they also are inclined to believe that strains due to the formation of the  $\text{CuAl}_2$  are not a significant factor in changing (in this case, increasing) the lattice parameters of the matrix solutions. They report that other authors have held different opinions.

While the possible effect on the lattice parameters of dispersion, interfaces and differential contraction of the two phases probably is smaller on the matrix solution than on the precipitated phase, the effect on the latter may be considerable. For the matrix, however, the effect certainly must approach zero as the proportion of the bulk of the dispersed phase approaches zero. Lattice parameters of predominantly one-phase alloys obtained on the usual fine powders, must therefore be considered essentially free from errors due to distortion. On the other hand, lattice parameters of a highly dispersed phase present in relatively small proportions in a matrix solution are probably functions of several other variables in addition to composition and temperature. It may be questioned whether under extreme conditions the strains may not be sufficient to so disarrange the lattice that the reflections will be entirely lacking.

#### THE PARAMETRIC SURFACES

The procedure of utilizing lattice parameters for the determination of solid solubility limits in binary systems is well established, (5) (6). The variation of lattice parameters with composition is plotted and the points at various temperatures at which the parameter size of the primary phase becomes constant with increasing percentage of the second metal are noted.

For ternary systems the procedure is identical in principle. However, the presence of a third component necessitates the use of one more concentration, and thus one more dimension in the diagram for the complete representation of the variables. Therefore, the variation in any characteristic property with composition must be represented by surfaces instead of lines and phase boundaries or solubility limits by intersections of surfaces instead of intersections of lines. Similarly, the variation of lattice parameter with composition throughout a solid solubility region will be represented by a surface, more or less resembling a melting point surface. Each point on the surface corresponds to a definite composition of the primary phase and its appropriate lattice parameter; horizontal sections through the

surface at stated intervals will then yield contour lines indicating compositions of constant parameters. We shall refer to such a surface as a "parametric surface" and to the contour lines as "isoparametric curves." The parameters<sup>3</sup> of any phase, of course, are a function of the coefficient of heat-expansion and temperature.

In multiple-phase regions conditions are different. For any given composition of an alloy within such regions the corresponding compositions of the primary phase are found not within the multiple-phase region but on its boundary with the primary-phase region, and this generally varies with temperature. Over a three-phase region the parametric surface for any fixed temperature becomes a horizontal plane since according to the phase rule the compositions of all three phases are invariant. The lattice parameter of this plane generally varies with temperature, and graphically corresponds with the composition of that one of the three corners of the region which lies on the primary-phase boundary. In a two-phase region the parametric surface is generally curved. Its horizontal sections, the isoparametric curves, become straight lines whose endpoints indicate phase compositions and are in all respects identical with tie-lines. The surface, of course, is variable with temperature.

The determination of solid solubility limits resolves itself into finding the intersections of the parametric surface of each single-phase region with those of adjoining two-phase regions at any desired temperature level. Where the approximate locations of solubility limits are known, their definite establishment requires only the determination of those portions of the parametric surfaces which cover the composition ranges lying in the neighborhood of the phase boundaries.

One of the most direct methods of finding the intersections between two parametric surfaces would be to lay out the systems of isoparametric lines for both the one-phase and two-phase regions. A point where the two parametric curves of the same parameter value corresponding to the two different regions intersect, would give one point on the boundary curve between the one-phase and two-phase regions. Since the parametric surface in the two-phase region changes with quenching temperature, the procedure would need to be repeated for each temperature. This method would require such a large number of alloys that it is generally not practical. For the

<sup>3</sup>Throughout this series of articles we follow common practice in using the terms "lattice constant" and "lattice parameter" synonymously although a body-centered lattice, such as alpha iron, has no "parameters" in the strict crystallographic sense.

same reason, methods based upon finding mathematical equations for the parametric surfaces and solving for their intersection must be discarded, even though the mathematical difficulties could be surmounted in some cases. With a folded surface, such as is obtained in the iron-chromium-silicon system in the alpha iron range, the mathematical difficulties are of no mean order.

### THE METHOD OF SECTIONS

The most practical way of dealing with the problem is to use the method of sections. In this case the variation of the lattice parameter with compositions is studied at compositions lying along a straight line drawn more or less arbitrarily across a portion of the triangular base diagram. Such a line is nearly always chosen so that (a) the percentage of one of the elements remains constant or (b) the ratio of the percentages of two of the elements remains constant. In either case, we may consider a section line as if it were a binary though the interpretation of the data differs from that for a true binary.<sup>4</sup> (6) (7).

At this point it will be desirable to discuss some of the various possible changes in the lattice constant as a phase boundary is crossed along a section line. Unlike binary systems, the lattice parameters will not, in general, remain constant with further change in composition after a phase boundary has been reached. On the contrary, they may increase, decrease or remain constant. When at a constant temperature level one moves from a single-phase area into a two-phase area which yields conjugate solutions, the functions giving the relationship between alloy compositions and lattice parameters of the primary phase will split up into two branches, which, however, in a rare, special case may coincide. Along an arbitrary section, such as M-a-b crossing the boundary line<sup>5</sup> (see Fig. 2), the compositions of the alloys are identical with the composition of the primary phase between M and a. Beyond a, there exist two solutions whose compositions lie on the intersections between the solubility boundary line and the proper tie-line. The lattice parameters of these conjugate

<sup>4</sup>Thus Elis Persson (7) has investigated a section of the Cu-Mn-Al alloys of constant ratio of Cu:Al with a content of Mn varying from 0 to 67 per cent.

<sup>5</sup>Lines inside the two-phase region in Figs. 2 to 4 are tie-lines; those outside this region are lines of constant parameter or isoparametric lines. The lowest lattice constant or parameter in Figs. 2 and 4 is assumed to be at the point M; in Fig. 3 the pure substance M has a lattice constant which is intermediate, the constants increasing as composition in the one-phase region move to the left and upward.

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solutions depend upon the directions of the tie-lines and the slope of the parametric surface of the primary phase.

On a section M-a-b, one branch will show an initial decrease and then an increase in the size of the parameters.

On section M-c-d there will take place an increase at a very small rate on one branch, and an abrupt increase on the other.

In special circumstances which are possible although not very likely to be met, both branches may coincide. This case demands a

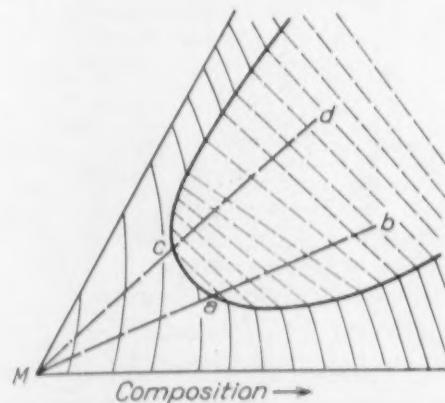


Fig. 2a

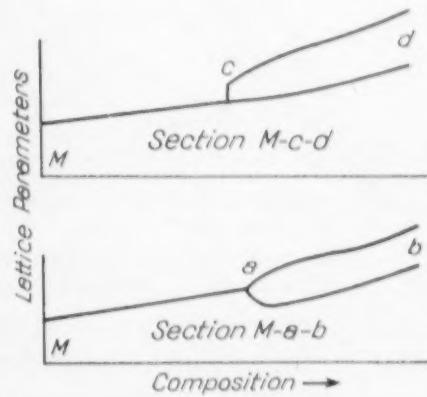


Fig. 2b

Fig. 2—Lattice Parameters Versus Composition; Conjugate Solutions.

certain symmetry in the tie-lines, such that they indicate pairs of terminal phases which, despite differences in composition, possess identical lattice parameters.

In a two-phase area where the phases are an intermetallic compound and the primary solid solution, the position of the section relative to a line connecting the primary phase corner and a point indicating the composition of the intermetallic compound, will determine the shape of the curves. On the line M-c-f (see Fig. 3) the lattice parameters will become constant upon crossing the phase boundary line. It is quite possible to have a case where the lattice parameters remain constant throughout both the single and the two-phase field. On the lines M-b-e and M-a-d, there may take place an increase on one and a decrease on the other, depending upon the slope of the parametric surfaces. With other courses of the equi-parametric curves, conditions may be such that for sections on either side of the line through the compound where the parameters remain constant on crossing into the two-phase field, either an increase on both sections may occur or a decrease on both sections. Such would be the case for conditions as shown in Fig. 4.

Conditions such as appear on section M-b-e (Fig. 3) are of special interest. The lattice parameters here decrease with additions to M of secondary elements. However, after passing into the two-

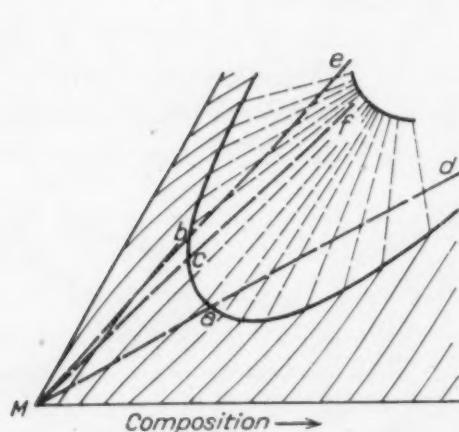


Fig. 3a

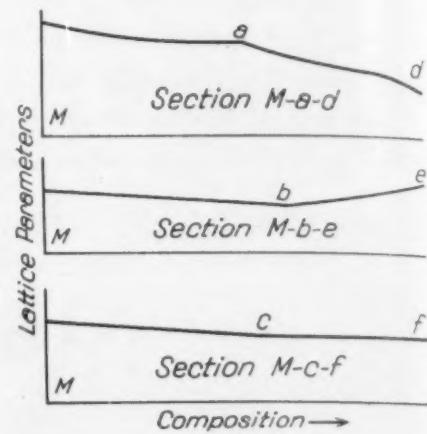


Fig. 3b

Fig. 3—Lattice Parameters Versus Composition; Compound Formation.

phase region an increase takes place. This would be unexpected from consideration of the two binaries alone. Presumably similar considerations apply to the variation with composition in other proper-

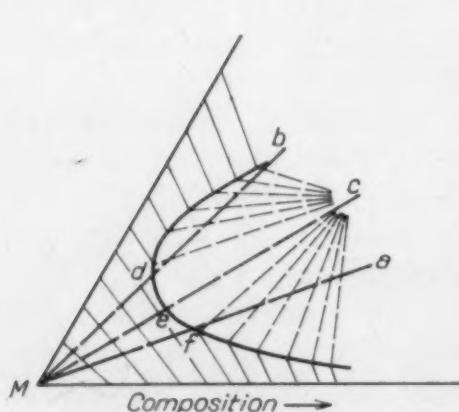


Fig. 4a

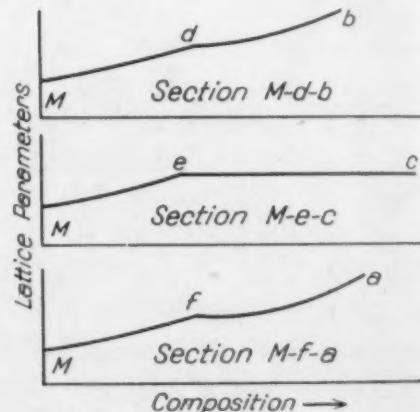


Fig. 4b

Fig. 4—Lattice Parameters Versus Composition; Compound Formation.

ties, as for instance electrical resistivity, despite the fact that such scalars involve the sum of those of each phase, whereas we are dealing separately with each phase in lattice parameter measurements. Consideration must then be given to the fact that conductivities decrease along both binaries.

**Table I**  
**Summary of Conditions Considered for Method of Sections**

- A. Two Conjugate terminal solid solutions
  - 1) Increasing parameters on both binaries
  - 2) Decreasing parameters on both binaries
  - 3) One binary shows increasing, the other decreasing parameters.
- B. A compound of fixed composition occurs, (with possibilities 1, 2 and 3, as stated under A.)
- C. A compound of variable composition, or a secondary solid solution occurs (with possibilities 1, 2 and 3 as above).
- D. Character of the secondary phase and its location on the diagram.
  - 1) A pure component, or a binary phase
  - 2) A ternary phase
- E. Character of Two-phase region
  - 1) Location
  - 2) Shape
  - 3) Size
- F. Position of section chosen
- G. Parametric surfaces, rates of variation of parameters with composition.
  - 1) A single phase parametric surface is generally a curved surface, which may or may not contain sections described by straight lines
  - 2) A two-phase parametric surface is, except in exceptional cases, a curved surface. Horizontal sections of this surface are straight lines synonymous with tie-lines
  - 3) A three-phase parametric surface is a plane.

Some caution should therefore be taken when dealing with essentially ternary alloys (or more complex systems) not to consider such variation abnormal without further consideration of the system as a whole. A knowledge of a considerable portion of the ternary diagram may be required to settle the question of what type of variation is to be expected.

The conditions may be hypothetically varied in many other details, and the directions of the sections altered. While it is naturally desirable to know something about the types of curves that one may meet with before starting experimental work, a detailed study of these can only be made after experimental facts have been collected. The most important of the conditions which must be considered are given in Table I.

#### METHODS OF DETERMINING PARAMETRIC SURFACES AND PHASE BOUNDARIES

In applying the method of sections it is, of course, essential to have a series of points situated on each section line. The accuracy with which they must approach the section line compositions depends upon the rate of variation of lattice constant with composition in the directions perpendicular to the section line; upon the accuracy of the lattice constant determinations; and upon the accuracy desired in the phase boundary determination. In many alloy systems, it is not

difficult to place alloys on the section lines with a high degree of precision. In others, such as the iron-chromium-silicon system, it is practically impossible to do so unless an extremely large number of alloys is made. Volatility of one or more of the constituents, losses by spattering, reaction with crucible material, etc., all affect the final composition of the alloys.

For these reasons it is necessary to develop methods of interpolation and extrapolation so that with a limited number of experimental observations, correction for the effect of deviations of actual composition from a given section line and extension into the regions of the phase boundaries will be possible. Recalling that a ternary system may be represented by a space model, our problem thus becomes to proceed from a limited number of known ordinates to the construction of some representation of the complete space model. It would be possible to build an actual model, say for the single phase region, in which case we would not be limited to extrapolations along section lines extending through the one-phase region into the two-phase region. Except in the case of a surface of very simple form, the labor of building such a model would be very great and much of the paper work to be described below would be necessary before the surface could be constructed with the required accuracy. The procedure to be used is essentially orthographic projection of a triangular prism with compositions along the base lines, and with lattice constants in the vertical direction. The approximate location of the various phase regions must be known from a few exploratory alloys, using the films to indicate the phases present. Such preliminary work is necessary if the section lines are to be chosen to the best advantage.

The first step involved is the preparation of a location diagram of all alloys in a system of components, A, B, C. Let A represent the predominant component, (or the solvent) of the alpha phase. In developing a representation of the single phase space, one begins by drawing a diagram representing the variation in lattice parameters with composition of both the binaries A-B and A-C. Next, on the location diagram a line of constant content of A is drawn in through any alloy. Where this line cuts the two binaries, ordinates representing lattice parameters are erected. Similarly an ordinate is erected through the given alloy composition. The last ordinate is known from direct measurement, and the other two may be read from their respective binary curves. We thus know three points on

the lattice parametric section of constant A content through the chosen alloy. By use of a large number of alloys we may obtain a large number of sections parallel to the B-C edge. On each section we know three ordinates. The lattice parameters versus composition on each section is then drawn in, one curve for each set of three points. We assume that no local variations in the parametric surfaces larger than the experimental error exist. Under this condition none of the sections of parameter versus composition should cross, and each curve is drawn so as to conform to the contours of the two or three nearest neighbors. Such a diagram is shown in Fig. 3 of our article on the Fe-Cr-Si phase diagram (Consult Reference 9). Finally, horizontal planes of constant lattice parameters are passed through this diagram with a convenient spacing apart, for instance 0.001 Å, the intersection of one such plane with the parameter versus composition for each section of constant A content gives a series of points of various compositions, determinable from the geometry of the diagram, which have equal lattice parameters. The compositions may then be laid out on a triangular composition diagram and connected by a smooth curve. We thus obtain an isoparametric curve. Repeating the process for all the lattice parameters, we obtain a set of horizontal sections or isoparametric curves, which adequately describe the parametric surface. From such a plot the parameter versus composition plot can be secured for any desired section line.

A similar method might be used for laying down the alpha-phase parameters in the two-phase regions, but this would require a large number of alloys throughout each of the two-phase regions, so that some modification of this procedure is desirable.

In order to determine the phase boundaries, it is sufficient to know with precision the parametric surfaces in the neighborhood of the intersections of the surfaces. It is advantageous to work with sections parallel to the binary edges. A number of planes are passed through alloy compositions in a two-phase region, parallel to edge A-C. Alloys which do not lie exactly on these sections may still be used to obtain ordinates corresponding to points located exactly on the sections, by means of interpolations. In order to interpolate it is convenient to draw in a vertical reference plane perpendicular to A-B. Through any alloy, a plane is passed parallel to A-B and perpendicular to the reference plane. A line parallel to A-B is obviously a section line along which the percentage of one of the com-

ponents is constant. Choosing such a section line on which we have two or more points, we now plot the lattice parameters of the alloys at their proper compositions. We repeat this for other section lines parallel to A-B and thus secure a family of lattice parameter versus composition curves. It is found that, unless there are local variations in lattice parameters greater than the experimental error, the curves have a general similarity of form, and never cross. With a little experience in using this method it is possible to secure this family of curves even if none of the sections has more than one alloy on it. The principle of general conformity of shape and direction of the curves may, of course, break down in special cases, since it is in effect assuming that the parametric surfaces vary continuously with composition. It is obvious that serious errors can be made if too few experimental points have been determined, but the minimum number of points required depends upon the nature of the system.

From this family of curves, points on any section parallel to A-C may be read off, and thus the experimental value for any alloy which lies somewhat removed from a section line parallel to A-B may be corrected back to the desired section.

Using this same family of curves, a plot is constructed to show the parameters versus compositions along a section parallel to A-C. From the plot of parametric surface in the one-phase region a similar curve is obtained along the same section line. The intersection of the curve from the two-phase area with the curve from the one-phase area gives one point in the phase boundary curve for the temperature to which the parameter measurements in the two-phase region correspond. In the same manner other phase boundary points on sections parallel to A-C are obtained and the whole phase boundary curve for this temperature is thus determined.

The accuracy with which phase boundaries can be determined by these methods depends very much upon the angle of intersection of the two parameter versus composition curves, as well as upon the accuracy of the parameters and compositions upon which the original curves were based. Small angles of intersection increase the uncertainty of the results. A description of the details of the procedure, together with illustrations using experimentally determined points, will be given in another article.

#### COMPOSITION OF SECONDARY PHASES

Location of the composition of secondary phases in ternary

systems may involve considerable labor. The "Klärkreuz verfahren" of Guertler (8) is of general utility. The definiteness and ease with which phases may be recognized by their photogram lines increase the advantages of this method, particularly for determination of the phases in three-phase regions. Approximate compositions may, however, sometimes be obtained from the same data which are used for locating the solubility limits. Occasionally, when the phase whose composition is to be determined is a binary compound of known structure, the process may resolve into a mere comparison of lines on the binary and the ternary photograms; even in such a case, however, computation of the size of the unit cell and density determinations may be required, in order to establish a limited substitution of a third element in the original binary cell.

In a two-phase field yielding conjugate solutions, their respective compositions are given by the intersection of the phase boundary line and the two parametric curves of the single phase field, which correspond to the two measured parameters of each alloy. The line connecting these two intersections must also pass through the point indicating the gross composition, thus giving a tie-line.

Where the secondary phase is itself a solid solution, the intersection with the phase boundary of the measured equiparametric curve of the primary phase in equilibrium may be connected by a tie-line through the point of gross alloy composition, and continued until it intersects the boundary curve of the secondary phase. Averaging and adjustments of the results may, of course, be required. These tie-lines, identical with isoparametric lines in the two-phase area, must necessarily be straight lines. If, therefore, the isoparametric curves in a two-phase area deviate from straight lines, or if they cross each other in an unsystematic fashion, it is certain that equilibrium has not been attained. Such a lack of equilibrium may be due to faulty technique in preparing the alloys, incomplete elimination of segregation, etc. However, it may be that the processes or reactions involved progress at rates so slow that the attainment of equilibrium requires inordinately long times of annealing. Complete equilibrium under such conditions may not be practically attainable. If some estimate of the effect on the determination of solubility limits, due to unstable conditions, can be formed, such a lack of equilibrium may not seriously affect the precision of the determination. A case of this kind was met in the investigation of the iron-chromium-silicon alloys.

When one of the phases in a two-phase region is a ternary compound, its composition may be estimated by a similar method. In this case, the composition of the primary phase in equilibrium is indicated by the intersection of the phase boundary line with the isoparametric line on the single-phase parametric surface, which corresponds to the measured parameter of the primary phase in the two-phase alloy. A line running from such an intersection point and through the point indicating the gross composition of the alloy is analogous to a tie-line. For the special case when the composition of the compound is invariable, all such lines must intersect in a point which will indicate the composition of the intermetallic compound. However, precision would require the use of a number of such tie-lines and of alloys placed at various points on the same tie-line. Where only a few alloys are available and where these are not in pairs located on the same tie-line, interpolations must be resorted to, and the location of the compound will be more or less uncertain.

Generally, the composition of an intermetallic compound in a two-phase region is variable, both with respect to temperature and to gross composition of alloy. At a given temperature, all the tie-lines will then traverse a two-phase area and be bounded by a second single-phase area. The disappearing phase criterion in conjunction with the degree of convergence of the tie-lines may be used to judge roughly the extent of this area. Although we have to do with a phase of variable composition, the simplest chemical formula which may be ascribed to any point located within the area consistent with the obtainable crystallographic information, may, for the sake of convenience, be assumed to be the formula of the compound. If the compound is not formed by a peritectic reaction, the final assignment of a chemical symbol should depend upon the location of a freezing point maximum within the area.

#### TEMPERATURE VARIATION OF LATTICE PARAMETERS IN TERNARY SYSTEMS

Determination of the temperature variation of solubility limits must be performed by comparing the changes in lattice parameters not only with temperature, but also with respect to alloy location on the coördinate system. In a section through a two-phase region, a change in lattice parameter of the primary phase does not neces-

sarily indicate a change in the solubility limit of this phase, unless the composition of the secondary phase is invariable or has compositions which vary in such a manner with temperature that the direction of the tie-line suffers no angular displacement with temperature.

In some binary systems the variation in lattice parameters with composition are too small to allow the solubility limits to be determined with sufficient precision. Westgren (6) has discussed such limitations of the X-ray technique. Application of this technique to ternary systems is subject to similar limitations. This may be the case even when both the limiting binaries show substantial rates of variation of lattice parameters with compositions. One soluble element added to a metal may increase its lattice parameter, while a second element decreases it. On some intermediate section the lattice parameters are liable to show very small rates of change; the section line, therefore, may also correspond to an isoparametric line. If the tie-lines between alloy compositions and the composition of the compound are nearly parallel to the isoparametric lines of the single phase field, the solubility limits may vary by large amount, although the measured lattice parameters show little or no variation. Under different conditions, a section which in the single phase field shows no variation in parameter with composition, may be suitable for the determination of solubility limits whenever the tie-lines intersect the isoparametric curves at substantial angles. Under such conditions the lattice parameters in the two-phase region will show variation with composition. In general, sections must be so chosen that they traverse a portion of the diagram on which the parametric surface in the single-phase region intersects the parametric surface in the two-phase region at a substantial angle. This is the only condition required and holds good even when the lattice parameters in the single-phase field show no variation with composition. It is, however, not always possible to fulfill this condition. In one portion of the phase boundary region it may be possible to obtain satisfactory intersections and in others not. The precision obtainable may therefore vary with composition, and the direction of the sections to be chosen also becomes important. Over a given portion of the diagram, sections taken in one direction may yield better results than sections taken in other directions.

Considerable probing is, therefore, necessary before the most favorable sections can be chosen. These considerations also make it evident that observations on an arbitrarily chosen single section oc-

casionally may be misleading. Only correlation of observations on a number of systematically placed alloys can give reliable information, even of an orienting and qualitative kind, of the temperature relation of solubility limits in a ternary system.

Correlation of observations made over a wide region may be very useful and facilitate interpolations so that a region can be investigated with a minimum number of alloys. Under ordinary conditions it can be assumed that the solubility limits at various temperatures are described with curves which conform to each other in shape or at least possess some systematic variation. This is not always true and the assumption breaks down when the change in solubility with temperature is very large. Under these conditions very little interpolation and still less extrapolation is permissible.

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## NOTES ON THE SOLIDUS TEMPERATURES IN THE SYSTEMS IRON-TUNGSTEN AND IRON-MOLYBDENUM

By W. P. SYKES

### Abstract

*By observations on the melting temperatures of wire specimens the solidus lines in the iron-rich portions of the iron-tungsten and iron-molybdenum binary systems have been located with seemingly increased precision.*

*Microstructures of small block specimens drastically quenched indicate that in both systems the alpha phase is formed as the product of a peritectic reaction: liquid +  $\epsilon \rightleftharpoons \alpha$*

SOME disagreements exist among the equilibrium diagrams of these binary systems as reported by several investigators. The bibliography of this subject is collected in the two volumes by Gregg (1)\* dealing with this group of alloys.

The diagram of the iron-tungsten system has been drawn in two forms. One shows the alpha solid solution forming a eutectic with the epsilon intermetallic phase. The other indicates the formation of the alpha phase as the product of a peritectic reaction between iron-rich liquid and solid epsilon. It appears that the first form has been favored by those who have studied the binary systems only. Investigators (2) of two ternary systems involving iron and tungsten have agreed upon the second form.

Uncertainty in the iron-molybdenum system has centered about the extent of the hypoeutectic concentration range. One obstacle common to both systems is the elevated temperature which renders especially difficult the determination of the solidus line by usual methods involving the use of thermocouples. A second obscuring factor is to be found in the high rate of decomposition of the alpha solid solution upon cooling. This is especially noticeable in the more concentrated alpha solid solutions of the iron-molybdenum system. Such alterations as have been made in the original diagrams appear

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\*The figures appearing in parentheses refer to the bibliography appended to this paper.

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to have resulted from scattered observations rather than from any systematic studies of the questionable fields in these alloy systems.

The present investigation was undertaken in hope of obtaining evidence which might establish with more certainty the forms of the solidus lines in these binary systems. So far as possible the solidus temperatures were determined by direct observation of wire specimens heated to fusion in a hydrogen atmosphere. Microstructures of specimens drastically quenched from temperatures near the solidus furnished further information bearing on the form of the diagram in this region.

#### THE IRON-TUNGSTEN SYSTEM

A series of iron alloys containing tungsten in percentages varying from 5 to 30 per cent was prepared by melting the pressed metal

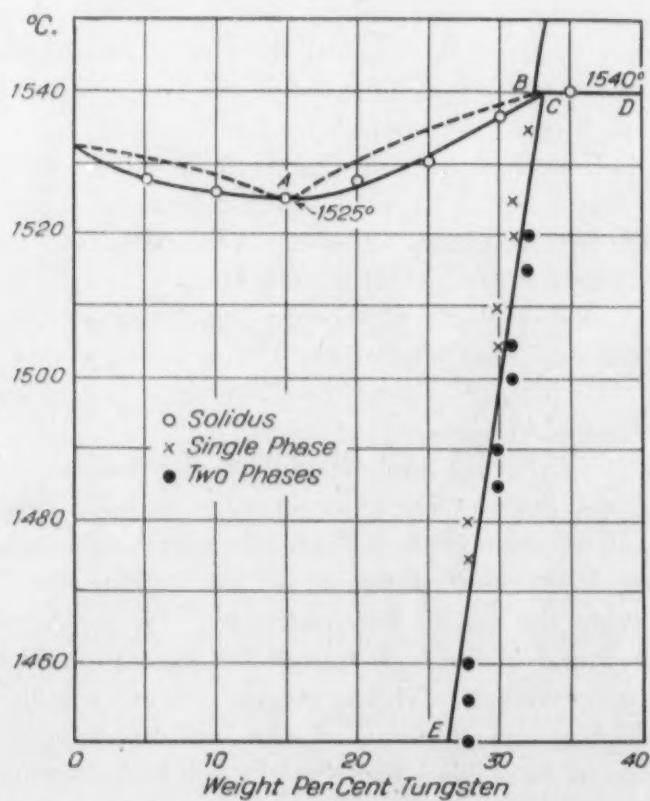


Fig. 1—Iron-rich Portion of Iron-tungsten Equilibrium Diagram.

powders<sup>1</sup> in the hydrogen atmosphere of a tungsten resistor furnace, the melts being contained in alundum boats. The resulting alloys

<sup>1</sup>The materials used in preparation of the alloys have been described in the original papers mentioned in foot note 1.

were hot-rolled, swaged and drawn into wires 0.025 inch in diameter. Chemical analyses of the product indicated that the compositions of the alloys varied by not more than 0.2 per cent from those indicated in the following diagrams.

Following the procedure outlined in a previous paper (3) the solidus temperatures were determined by observing the melting temperatures of the wires in this series, the melting point of pure iron being considered as 1532 degrees Cent. (2790 degrees Fahr.). As indicated in Fig. 1 a distinct minimum in the solidus occurs at about 15 per cent tungsten. Between 10 and 15 per cent tungsten the slight difference in melting temperatures could not be determined quantitatively, but when wires of those compositions were heated side by side the higher tungsten alloy was always the first to fall from a vertical position. Temperatures as shown in the diagram are placed at the midpoint of a 6-degree Cent. range within which the observed melting of a given composition was observed to occur in repeated runs.

Alloys containing more than 30 per cent tungsten could not be drawn into wire as small as desired. For the solidus determinations of such compositions it was necessary to examine the microstructures of quenched specimens. Such specimens about  $\frac{3}{8}$  inch square and  $\frac{1}{16}$  inch thick, from alloys previously prepared by melting, were slowly heated to the desired temperatures in the hydrogen atmosphere and quenched in a 10 per cent solution of potassium hydroxide which had been chilled to about 5 degrees Cent.

Chemical analyses of the two alloys which bracketed the end of the peritectic line showed tungsten contents of 32.3 and 32.4 per cent respectively. The values 32 and 32.5 per cent tungsten are used in the discussion, however, as being more in keeping with the degree of precision represented by the temperature measurements.

Until the tungsten content exceeds 32 per cent the microstructures observed after quenching from just below the solidus consist of the alpha solid solution only. At 32.5 per cent tungsten the epsilon phase ( $Fe_3W_2$ ) as a primary crystal first appears concurrently with alpha, the latter having been almost completely preserved by drastic quenching from 1540 degrees Cent. (2805 degrees Fahr.). These structures are illustrated in Figs. 2 and 3.

If, instead of quenching, these alloys are cooled from 1500 degrees Cent. (2730 degrees Fahr.) to black in two or three minutes epsilon separates from the alpha solid solution in the form of fine

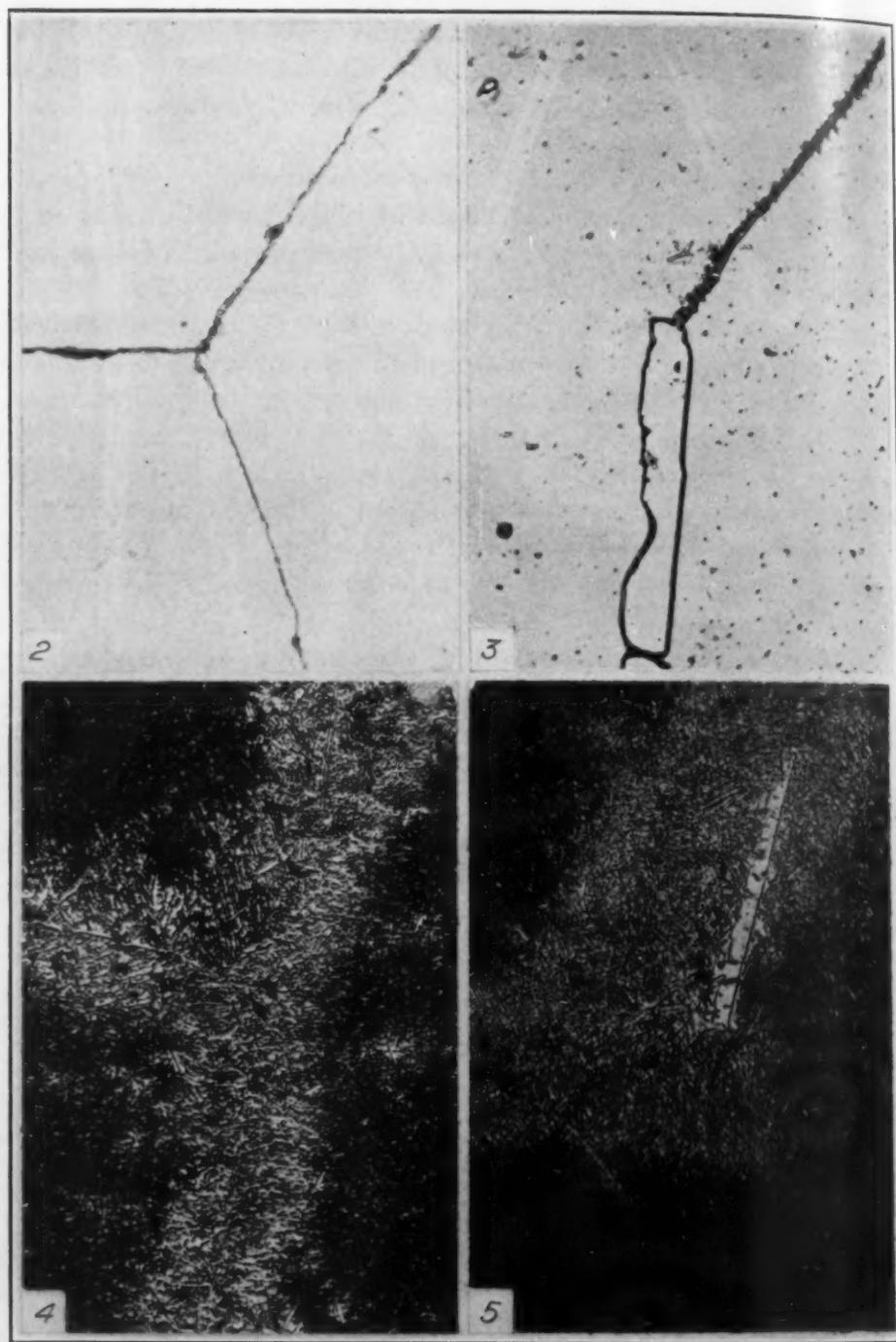


Fig. 2—Iron + 32 Per Cent Tungsten. Quenched from 1535 Degrees Cent.  $\times$  500. Etching reagent, 1 part  $H_3PO_4$ , 4 parts  $H_2O$ .

Fig. 3—Iron + 32.5 Per Cent Tungsten. Reheated 1535 to 1545 Degrees Cent. in 30 Minutes and Quenched.  $\times$  500.

Fig. 4—Iron + 32 Per Cent Tungsten. Melt Cooled from 1600 to 1500 Degrees Cent. in 5 Minutes; from 1500 to 600 Degrees Cent. in 3 Minutes.  $\times$  200.

Fig. 5—Iron + 32.5 Per Cent Tungsten. Melt Cooled from 1650 to 1500 Degrees Cent. in 5 Minutes; from 1500 to 600 Degrees Cent. in 3 Minutes.  $\times$  200.

plates or needles as shown in Figs. 4 and 5. The primary epsilon crystals become more numerous as the tungsten content increases above 32.5 per cent. Due to the relatively high density of this phase the crystals tend to segregate in the lower portions of the melt, and in alloys containing more than 35 per cent tungsten it is difficult to prevent such segregation even by agitation and rapid freezing.

The structures indicate that the alpha solid solution is the

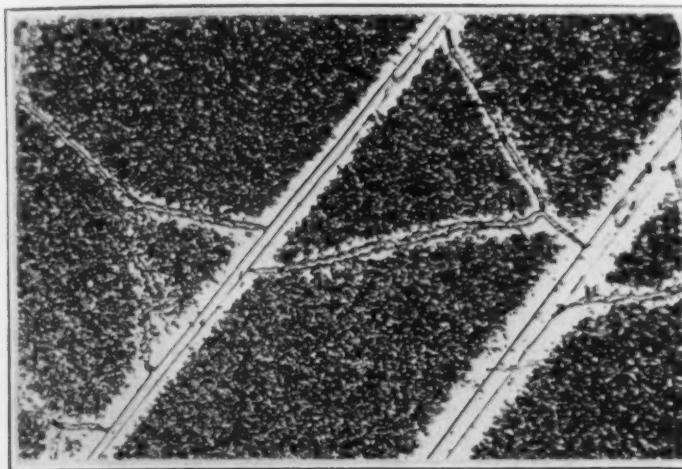


Fig. 6—Iron + 33 Per Cent Tungsten. Melt Cooled Rapidly from 1650 to 600 Degrees Cent. Then Reheated at 1520 Degrees Cent. for 1 Minute and Quenched.  $\times 200$ .

product of a peritectic reaction at about 1540 degrees Cent. (2805 degrees Fahr.) between primary epsilon and iron-rich liquid, and the diagram in Fig. 1 is drawn accordingly.

Unless preserved by a drastic quench, the alpha phase, especially when nearly saturated in tungsten, will decompose yielding a duplex structure which has been mistaken for that of a eutectic.

No evidence was noted of a reaction zone surrounding the primary epsilon. Since the product of the reaction differs so slightly in composition from the liquid phase such a zone might reasonably be indiscernable in the microstructure. In an alloy cooled less rapidly there appears a border of clear alpha about the primary epsilon, as in Fig. 6. This, however, is presumably the commonly observed "grain boundary effect".

The limit of the alpha field between 1100 and 1530 degrees Cent. (2010-2785 degrees Fahr.) was determined by observation of structures in a group of compositions quenched from a series of increasing temperatures. In Fig. 1 this line CE, so obtained, is in

accord with the foregoing data as regards the peritectic temperature and the composition of the alpha phase formed by this reaction. From about 33 per cent tungsten at 1540 degrees Cent. (2805 degrees Fahr.) the alpha boundary recedes to 12 per cent tungsten at 1100 degrees Cent. (2010 degrees Fahr.) according to the microstructures observed in quenched specimens. At 700 degrees Cent. (1290 degrees Fahr.) the boundary lies between 6 and 7 per cent tungsten as indicated by measurements of electrical resistance.

### THE IRON-MOLYBDENUM SYSTEM

Alloys in this system containing more than 20 per cent molybdenum are difficult to work into small wires probably on account of the hardening which accompanies the rapid decomposition of the

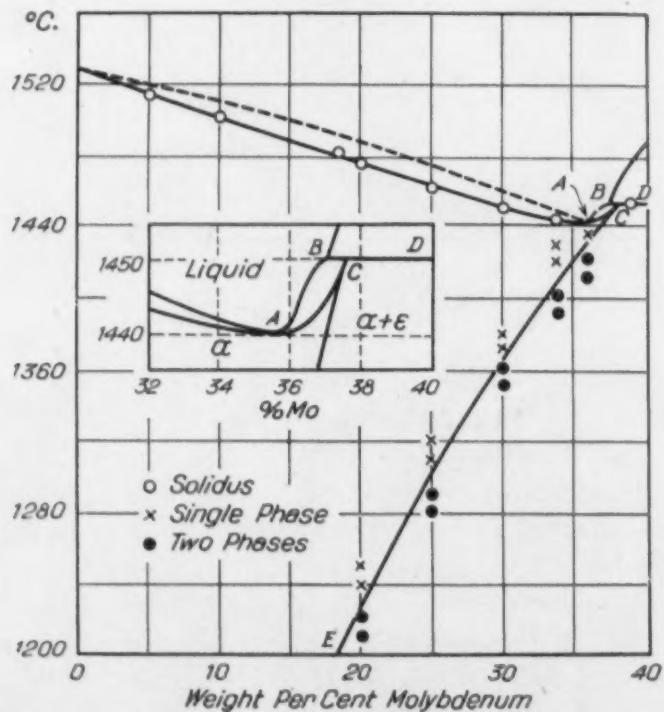


Fig. 7—Iron-rich Portion of Iron-molybdenum Equilibrium Diagram.

alpha solid solution at lower temperatures. Consequently, specimens of higher molybdenum content used for the solidus determinations were obtained by shaping pins of the desired size from the cast alloys.

As drawn in Fig. 7 the solidus temperature falls steadily to a minimum of  $1440 \pm 3$  degrees Cent. at about 36 per cent molybdenum. Repeated comparisons of the 34 and 36 per cent alloys

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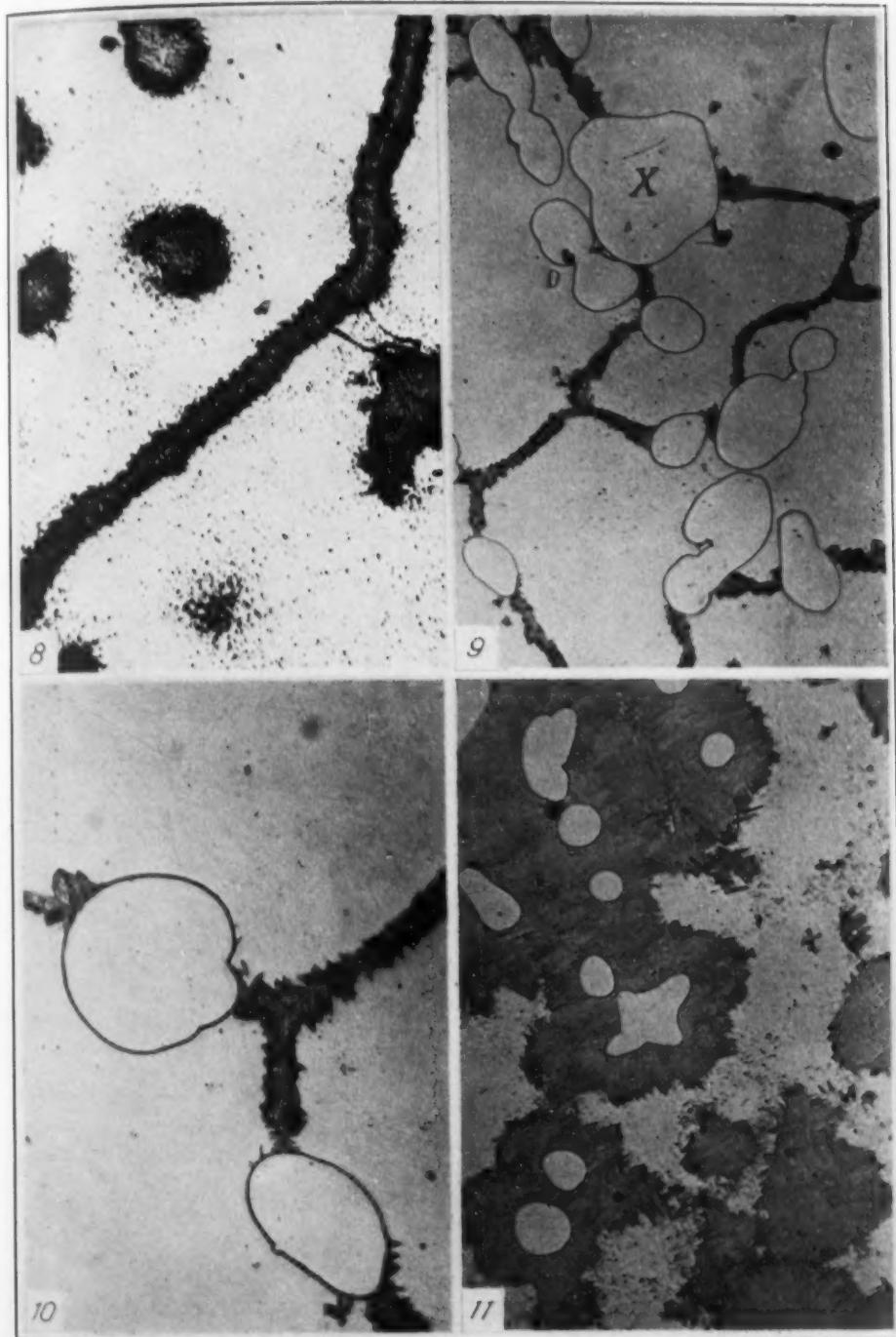


Fig. 8—Iron + 36 Per Cent of Molybdenum. Heated from 1430 to 1445 Degrees Cent. in 20 Minutes and Quenched in 10 Per Cent KOH at 5 Degrees Cent.  $\times 200$ .

Fig. 9—Iron + 38 Per Cent Molybdenum. Heated from 1430 to 1455 Degrees Cent. in 50 Minutes and Quenched in 10 Per Cent KOH at 5 Degrees Cent.  $\times 200$ .

Fig. 10—Same as Fig. 9.  $\times 500$ .

Fig. 11—Iron + 38 Per Cent Molybdenum. Heated from 1430 to 1455 Degrees Cent. in 20 Minutes and Quenched in Water at 15 Degrees Cent.  $\times 200$ .

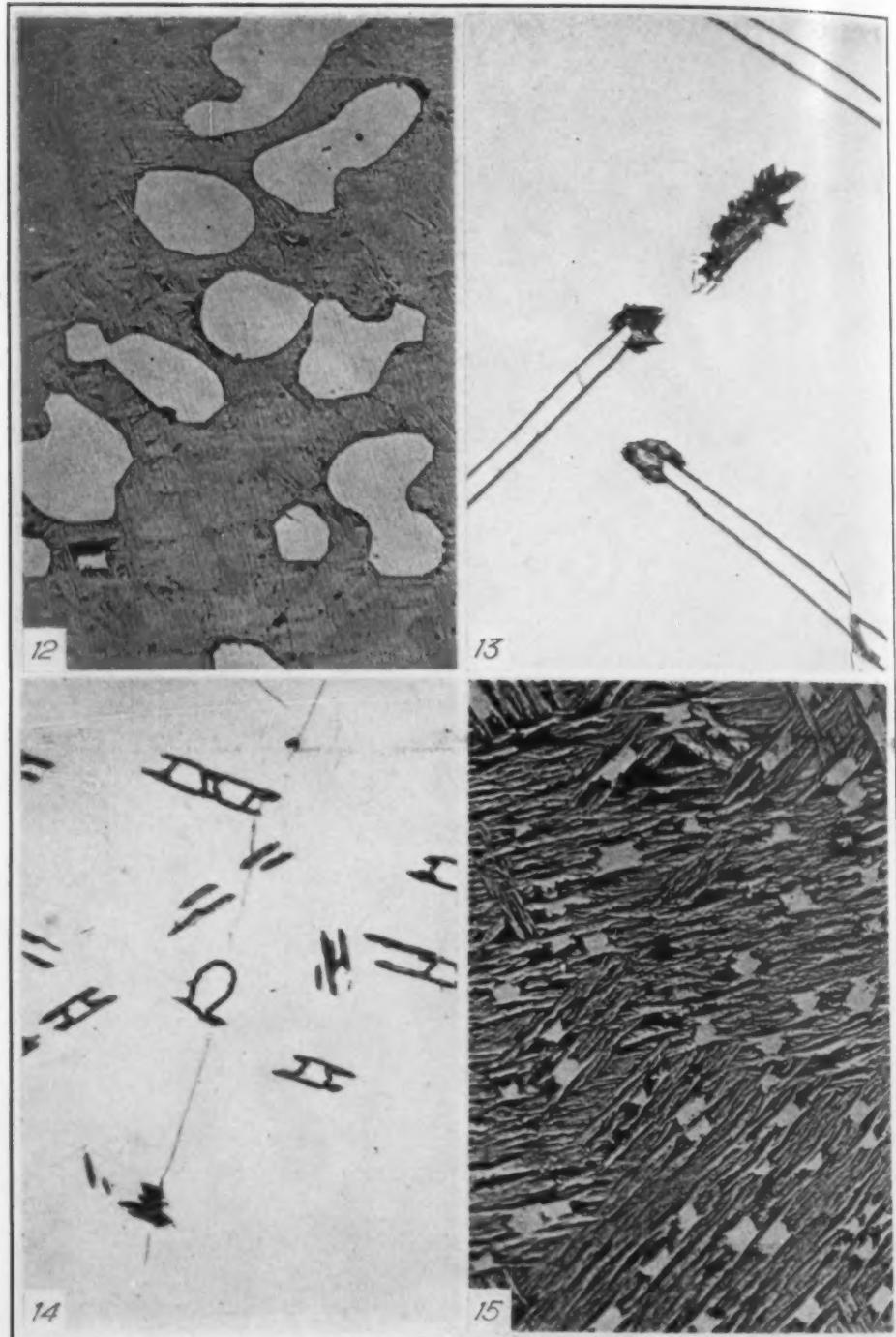


Fig. 12—Iron + 38 Per Cent Molybdenum. Cooled from Melt, 1475 to 1440 Degrees Cent. in 20 Minutes. Quenched from 1440 Degrees Cent. in Water at 15 Degrees Cent.  $\times 200$ .

Fig. 13—Iron + 36 Per Cent Molybdenum. Reheated 1420 Degrees Cent. for 30 Minutes. Quenched in 10 Per Cent KOH at 5 Degrees Cent.  $\times 500$ .

Fig. 14—Iron + 36 Per Cent Molybdenum. Reheated 1420 Degrees Cent. for 30 Minutes. Quenched in 10 Per Cent KOH at 5 Degrees Cent.  $\times 500$ .

Fig. 15—Iron + 36 Per Cent Molybdenum. Reheated 1350 to 1430 Degrees Cent. in 25 Minutes. Quenched in Water at 15 Degrees Cent.  $\times 500$ .

indicated a slightly lower solidus temperature for the latter composition.

Primary epsilon ( $Fe_3Mo_2$ ) first appears in compositions between 36 and 38 per cent molybdenum as may be seen in Fig. 9 in which the epsilon is marked (X). The formation of liquid upon reheating the 36 per cent molybdenum alloy results in the dark etching network of finely meshed epsilon shown in Fig. 8. This formation will also be observed at the grain boundaries of the 38 per cent alloy in Fig. 10. An appreciable quantity of primary epsilon appears in the latter structure along with alpha.

The primary epsilon in Figs. 9 and 10 has lost its dendritic outline due to prolonged heating near the peritectic temperature. In Fig. 11 however, the original shape is more perfectly preserved. This structure illustrates, as well, the inability of a less drastic quench to preserve the alpha from decomposition during cooling. In Fig. 12 is shown a specimen of the 38 per cent alloy which was water-quenched from below the solidus. Precipitation of epsilon in a closely meshed form has occurred throughout the alpha which surrounds the primary epsilon areas. Most of this precipitation probably occurred while the alloy cooled from 1450 to about 1440 degrees Cent. (2640-2625 degrees Fahr.), previous to the quench.

Apparently the alpha phase is formed by a peritectic reaction in this system as in the iron-tungsten system. The structure resulting from the alpha decomposition was originally mistaken by the author (4) for that of a eutectic. Takei and Murakami (5) subsequently interpreted the structure correctly, but assumed that a eutectic did exist in the system with a hypoeutectic range extending from about 38 to some 40 per cent molybdenum.

Unusual formations of the epsilon precipitate are often observed, three instances of which are illustrated in Figs. 13, 14 and 15. In the first two microphotographs epsilon appears to have separated from the alpha solid solution during the quench in areas adjoining the residual epsilon needles and globules. In Fig. 15 some of the epsilon plates which had formed at a temperature well below the limit of the alpha field have responded to a "spheroidizing treatment" by assuming a rectangular outline.

Between the temperatures of 1430 and 1130 degrees Cent. (2605-2065 degrees Fahr.) the molybdenum concentration of the saturated alpha phase decreases from 36 to 15 per cent as determined by the microstructures of quenched specimens. Resistance measure-

ments indicate that at 700 degrees Cent. (1290 degrees Fahr.) the limit of the alpha field lies between 3 and 5 per cent molybdenum.

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## SOME TRANSIENT PHASE CHANGES DURING THE GRAPHITIZING REACTION

By H. A. SCHWARTZ, H. H. JOHNSON AND C. H. JUNGE

### Abstract

Using certain data and material kindly furnished by Cyril Smith and Earl W. Palmer of the American Brass Company, the authors have attempted to follow the changes in composition and specific volume of the cementite and solid solution phases during the process of graphitization in the light of their own metallographic and density investigations.

It appears that material partially graphitized at 925 degrees Cent. (1700 degrees Fahr.) is converted on cooling and holding below  $A_1$  into graphite plus  $Fe_3C$  plus decomposed solid solution (granular pearlite) of approximately metastable eutectoid composition. At the elevated temperature, however, the cementite decreases progressively in carbon content and increases in density; the latter remaining a simple function of the former. The stable solid solution saturated at 925 degrees Cent. (1700 degrees Fahr.) is less dense than the saturated metastable solution by about 1 per cent.

ONE of the present authors (1)<sup>1</sup> in co-operation with others has suggested that there must be two solid solutions of carbon in iron depending upon whether the equilibrium is with cementite or carbon and has suggested the name Boydenite for the latter. Reasons have also been given (2) for considering that the difference may reside in the location of the carbon atom in the gamma lattice. It was later shown (3) that even the cementite phase does not remain unaltered in composition during graphitization. Quite lately a demonstration has been furnished (4) that the expansion of white iron during graphitization is not a linear function of the amount of graphite formed and hence that there must exist changes of density in the metal matrix during the process of graphitization. Assuming, as seems reasonable, that this phenomenon is general and not

<sup>1</sup>The figures in parentheses refer to the bibliography appended.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago the week of September 30 to October 4, 1935. Of the authors, H. A. Schwartz is manager of research and H. H. Johnson and C. H. Junge, members of research staff, National Malleable & Steel Castings Co., Cleveland. Manuscript received May 18, 1935.

limited to the presence of copper, we may use the observations of Smith and Palmer to gain some insight into the changes going on during graphitization.

The iron used by Smith and Palmer had a composition as follows:

Carbon	2.40	Per Cent
Silicon	1.01	Per Cent
Manganese	0.31	Per Cent
Phosphorus	0.144	Per Cent
Sulphur	0.075	Per Cent
Copper	1.33	Per Cent

being alloy 1652 of their publication. It is to be noted that this analysis does not check the carbon content of any of the subsequent data but this is a point of little consequence since we use throughout the actual carbon content of the samples under discussion.

Smith and Palmer have kindly elaborated on the original publication in private correspondence and give the data of Table I together with the following explanations which are quoted verbatim with some omissions of matter irrelevant to the present discussion as follows: "Because of the few specimens we had available, and

Table I

Spec. No.	Time at 925°C. Min.	Total Carbon Per Cent	Graphitic Carbon Per Cent	Combined Carbon Per Cent	Fe <sub>3</sub> C Graphitized Per Cent		Per Cent Expansion	Expansion of 4.5 Inch Specimen Inch
					Comple- tion Per Cent	Analysis		
1652-M1	0	2.48	0.063	2.42	0.063	4	0	0.0000
	42	2.47	0.49	1.98	0.50	36	25	0.0100
	61	2.45	1.03	1.42	1.06	76	50	0.0200
	145	2.44	1.30	1.14	1.34	96	87½	0.0350
	310	2.41	1.33	1.08	1.40	100	100	0.0400
1652-M6	0	2.45	0.02	2.43	0.02	1	0	0.0000
	42	2.47	0.54	1.93	0.52	40	25	0.0100
	61	2.43	0.82-0.83	1.60	0.85	66	50	0.0200
	100	2.42	1.19	1.23	1.22	95	75	0.0300
	310	2.34	1.18	1.16	1.29	100	100	0.0400

All specimens heated to 925 degrees Cent. (1700 degrees Fahr.) in 2.7 hours.  
Oxidation losses assumed to affect graphitic carbon only.

the difficulty of quenching from the dilatometer, the specimens used for analyses and micros were  $\frac{3}{4}$  inch pieces of the white iron bars used for dilatometer specimens. These were heated in the dilatometer tube for times corresponding to various percentages of the expansion observed on another specimen of the same iron. That is, the expansion of the sample analyzed was not directly observed. As a matter of fact, two sets of samples were run, and the lack of agreement

between the two convinced us that the results were only qualitative in nature. A  $\frac{1}{4}$ -inch slice was sawed from each sample and the inside face polished for microscopic examination, while the larger piece was sampled for analysis by drilling two  $\frac{3}{16}$ -inch holes completely through after the slightly decarburized skin had been ground off. The drillings were quite fine, short chips, with little graphite dust, and after thorough mixing were used for total carbon and graphitic carbon determinations. While we agree that sampling errors were probably somewhat larger than would be the case with a solid sample, it seems doubtful if any serious error is involved. Duplicate graphitic carbon determinations were run on one of these samples (1652-M8) with an excellent check.

In annealing these specimens, the whole group was placed in the bottom of a 1-inch closed end silica tube, with several disks of graphite strung along the tube to serve as baffles and maintain a reducing atmosphere closely reproducing that obtained in the dilatometer. Specimens were removed and quenched after stated times, and were then reheated  $\frac{1}{2}$  hour at 650 degrees Cent. (1200 degrees Fahr.). This was done to soften the specimens for cutting off the micro sample, and also to give a dark-etching background against which cementite could be readily identified. We believe that the brief treatment at 650 degrees Cent. (1200 degrees Fahr.) caused no additional graphitization, and the analyses should not be affected.

Each sample was analyzed for total carbon and for graphitic carbon, the difference between these figures being the reported combined carbon content. However, the total carbon figure decreased with increasing times of anneal, indicating some oxidation during the treatment, and in order to secure a better measure of the "Fe<sub>3</sub>C graphitized," the "combined carbon" figure of each sample was subtracted from the "total carbon" content of the specimen held for zero time at 925 degrees Cent. (1700 degrees Fahr.) — a procedure which involves the assumption that oxidation affected the graphite determination only. . . . The expansion of the alloy from room temperature to 925 degrees Cent. (1700 degrees Fahr.) for a heating time of 2.2 hours (practically the same for 2.7 hours) varied slightly from specimen to specimen — presumably due to differing rates of cooling, etc. of the casting. For the specimens from which the expansion data were taken the total expansion of the 4.5-inch specimen, to 925 degrees Cent. (1700 degrees Fahr.) was 0.0622 inch. Other specimens were within  $\pm 0.002$  inch of this value. This com-

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parison of expansion and graphite formation is at best very approximate, because the expansion of the analyzed samples was not actually determined.

They have also furnished us their original metallographic specimens whose density we determined by the Archimedean method. Micrographs were made in four areas for each specimen and the (volume) fraction of the material composed of cementite was measured on the intercept planimeter in the usual manner. The density of specimen 1652-M4 is apparently in error. The presence of an internal void is suspected. In measuring the cementite the intention was to exclude only the carbide which had apparently been in solution at high temperatures but to include small, often spherical, remnants which evidently were present at high temperature. Our data are shown in Table II.

Table II

Specimen	Density gm/cm <sup>3</sup>	Volume Per Cent Carbide	
		Total Volume	Volume Metal Matrix
1652-M1	7.695	22.1	22.1
M2	7.621	21.4	21.8
M3	7.548	11.4	11.8
M4	7.439	2.7	2.8
M5	7.486	0.4	0.4
M6	7.704 and 7.695	20.7	21.1
M7	7.626	17.1	17.5
M8	7.565	14.5	14.8
M9	7.509	5.7	5.9
M10	7.490	0.2	0.2

Although Smith and Palmer regard cementite as practically absent in M5 and M10, this is not rigidly true. We point to this fact in demonstration of our oft repeated warning that the disappearance of primary cementite is a very insensitive means of deciding when the "first stage" graphitizing action is complete.

In connection with the following treatment of the available data we must absolve Smith and Palmer from any responsibility in connection with errors of judgment or interpretation. The data can be evaluated as follows: We know the density and hence the specific volume, at room temperature, of the but slightly graphitized material at the beginning of graphitization, since we know the expansion in heating to 925 degrees Cent. (1700 degrees Fahr.) we know also the specific volume at 925 degrees Cent. and since we know the expansion at 925 degrees Cent. of the specimens which have been partially graphitized we can compute their specific volumes if we as-

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sume no loss of weight or if, alternatively, we consider the weight to be reduced by the amount of decarburization. It is not certain whether the apparent decarburization is actually due to oxidation or whether it is due to loss of graphite in sampling. It will appear later that we do not have to be careful in our choice for the resulting difference is insignificant except in one case.

Since we know the graphite content (in choosing either the reported values or the value which Smith and Palmer call  $Fe_3C$  graphitized according to the choice we have made in the matter of loss of weight) and since the density of graphite at 925 degrees Cent. (1700

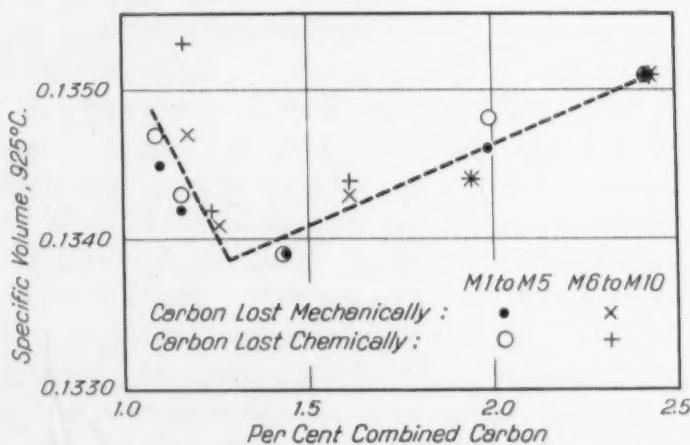


Fig. 1—Relation of Combined Carbon to Specific Volume at 925 Degrees Cent. (1700 Degrees Fahr.) of the Metallic Matrix of Partially Graphitized White Cast Iron.

degrees Fahr.) is possibly 2.20 (5) we can compute the volume of graphite in a gram of alloy and hence also the volume of metal by deducting the graphite volume from the specific volume of the alloy. We know the weight of metal per gram of alloy for it is one gram less the weight of graphite considered present and hence we can calculate the specific volume of the metallic portion of each alloy. These values have been calculated and plotted in Fig. 1 against the combined i.e., agraphitic carbon content of the metal of the alloy i.e., the observed "combined" carbon divided by 1 less the amount of graphite considered present.

The metal of the alloy consists, at 925 degrees Cent. (1700 degrees Fahr.) of two phases, cementite and solid solution. If these remained unaltered in composition and structure, the cementite merely being converted into iron and graphite and the iron so formed saturating itself at the expense of more cementite or some graphite,

there should be a rectilinear relation of agraphitic or combined carbon to specific volume. This is not the case as was already pointed out by Smith and Palmer on the evidence of a lack of proportionality between graphite formed and expansion.

The data may, however, be represented by two straight lines without any great contradiction except for specimen M10 if the carbon loss be deemed chemical. For the moment we offer the two dotted lines of Fig. 1 only tentatively as illustrative of what might be going on. The simplest though not the only explanation of such a locus is that below 1.20 per cent combined carbon; the metal matrix consists of one pair of phases and above that value, of another. If the representation of Fig. 1 is justified and if we may assume that the solubility of carbon from graphite is a little over 1 per cent at 925 degrees Cent. (1700 degrees Fahr.) and about 1.25 per cent from cementite as they would be if no copper or silicon were present, then the specific volume of the solid solution of the stable system will be about 0.1351 and of the metastable system about 0.1338 and the break comes very nearly at the point corresponding to the concentration of carbon in saturated austenite. An extrapolation to the specific volume of cementite can be made which leads to a specific volume of cementite of 0.1398 if the carbon concentration be 6½ per cent as is classically assumed. Correcting these densities for a thermal expansion of 4 per cent assumed to apply equally to all phases we obtain the densities of Table III, the solutions being saturated at 925 degrees Cent. (1700 degrees Fahr.).

Table III

	Stable Solution	Metastable Solution	Cementite
Specific Volume at 925 degrees Cent. (1700 degrees Fahr.)	0.1351	0.1338	0.1398
Density at 925 degrees Cent. (1700 degrees Fahr.)	7.40	7.47	7.15
Density at 26 degrees Cent.	7.70	7.77	7.43

All of these results are at least possible. An extrapolation for the density of the carbide phase present below 1.25 per cent combined carbon becomes quite uncertain for we do not know much about its possible composition. If the carbon content be that of cementite, a specific volume of 0.1063 is indicated if it be around 9 per cent, for which there is some evidence in the reference, it should be about 0.0935. In either case remarkably high values near 11 are obtained for the densities at room temperature. Since there seems to be little

likelihood that any arrangement of iron and carbon atoms in space could be enormously denser than austenite; the steep slope of the line in this region points to the presence of a relatively low carbon cementite such as is described in the references as occurring at high temperatures. Furthermore, if the carbon content of the cementite existing during the beginning of the graphitizing reaction be higher than the usual 6.7 for which viewpoint there is much support in the references, then its density is lower than that of orthodox cementite which in the demonstrated absence of expansion (at least after

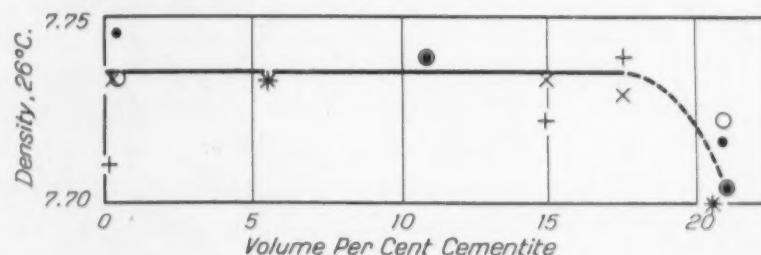


Fig. 2—Relation of Density to Volume Per Cent of Cementite at Room Temperature of the Metallic Matrix of Partially Graphitized White Cast Iron.

quenching) of the cementite lattice points to a substitutional solution of carbon in cementite confirming on the basis of observation the conjecture (3) that the solution might be substitutional.

If we plot the data derived from the observed densities in their final room temperature conditions of the several specimens as a function of cementite content, a nearly horizontal straight line is obtained, there being but a slight increase of specific volume with agraphitic carbon content and no discontinuity. One need not, therefore, assume that the compositions of the cementite and the transformed solid solution are not the same throughout the series or that their densities are very different.

In Fig. 2 the densities of the metal matrix, calculated from the density of graphite at room temperature, 2.25 (5) the observed amount of graphite and the measured density are plotted against the observed percentages by volume of cementite. One observes that, except for M1, M2 and M6, the densities are as well represented by a horizontal line at a density of 7.735 as by any other locus. M4 is omitted because of the apparent error already referred to. One can hardly say what the curve should be to the right of 17.5 per cent cementite. It is represented in the figure by a dotted curve of no particular significance. There might, for example, be a discon-

tinuous change at some point between 17.5 and 20 per cent. The horizontal line probably can have but one significance, namely that the density of cementite and of decomposed solid solution in the samples at room temperature is identical except above 20 per cent cementite. This having been demonstrated, the combined carbon content of the metallic matrix should be a straight line if the cementite and solid solution are of constant composition in all the samples.

Fig. 3 representing a plot of combined carbon against volume per cent cementite shows that with the exception of the initial samples

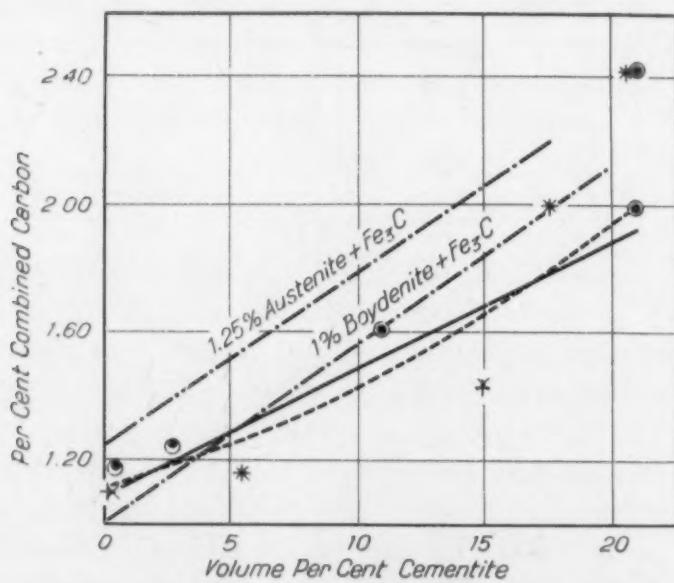


Fig. 3—Relation of Combined Carbon to Volume Per Cent of Cementite at Room Temperature of Metallic Matrix of Partially Graphitized White Cast Iron.

M1 and M6, none of the data fall on the composition corresponding to mixtures of 1.25 per cent carbon in the (decomposed) austenite and  $Fe_3C$ , both being assumed to have the same density and but little better on the line representing a mixture of 1 per cent carbon, Boydenite and cementite. The heavy straight line is, perhaps, as nearly a compromise for all the points as is any curved line that could be drawn such as, for example, the dotted line of Fig. 3. If the straight line is to be taken as representative of the relationship, then the solid solution contained before transformation, about 1.10 per cent combined carbon and the cementite contained the carbon content at which the line extrapolated toward the right, cuts the ordinate at 100 per cent cementite, which is about 4 per cent.

If the dotted line is taken to represent the facts better, then the final value of combined carbon is obtained by extending the tangent to the curve at cementite = 0 until it intersects the ordinate cementite = 100 at about combined carbon 3.50 per cent. For intermediate stages of graphitization the composition of the solid solution and cementite are given by the intersection with the zero and 100 ordinates of a line tangent to the curve at the existing cementite percentage. The combined carbon in the solid solution would then fall and that of the cementite rise as one approached the starting point of graphitization. There are obvious difficulties with any assumption of a lower combined carbon than the solubility of carbon in Boydenite at 925 degrees Cent. (1700 degrees Fahr.). It is, of course, possible that some decrease brought about during the heat treatment below  $A_1$  after previous quenching would accelerate subsequent graphitization (6).

The curve we have drawn has no significance beyond its own terminus and there requires a combined carbon in the decomposed solid solution of about 0.80 per cent and in the cementite of about 7 per cent, results which after all are not so wildly impossible as to be meaningless. The point for M2 is not far removed from any line which can be drawn through the other points, except M1 and M6, and since it also falls near the 7.335 density line in Fig. 2, it is possible that it should be included with the later points. In the literature (3) quoted a value above 8 per cent is indicated as a probable initial value of carbon in cementite after quenching. We may be confronted with a mere inaccuracy of extrapolation, an effect of copper, an effect of subsequent heat treatment after quenching or a decrease in cementite carbon content with progressing graphitization. Attention is invited to the fact that although it is the universal observation (7) that the volume of cementite decreases at the beginning of graphitization before any substantial amounts of graphite are liberated; the reverse is the case when M1 and M2 are compared. One is strongly inclined to suspect that at such temperatures as here used in tempering rearrangements take place below  $A_1$  which obliterate the condition normal for 925 degrees Cent. (1700 degrees Fahr.). Figs. 2 and 3 must be read as applying to compositions in the "as is" condition and not rashly extended to what may have been at 925 degrees Cent. (1700 degrees Fahr.).

Further evidence that the volume relations of cementite and solid solution existing at 925 degrees Cent. (1700 degrees Fahr.)

are not maintained in the specimens in their present condition may be had by evaluating the density and combined carbon data at 925 degrees Cent. (1700 degrees Fahr.) in relation to the existing volume relation. Figs. 4 and 5 show the relation of density and *carbon per unit volume* to the volume percentage of cementite. If the solution and cementite phases were the same throughout the graphitizing process both the locii would be straight lines. Being curved, the partial properties of the two phases at a given cementite content may

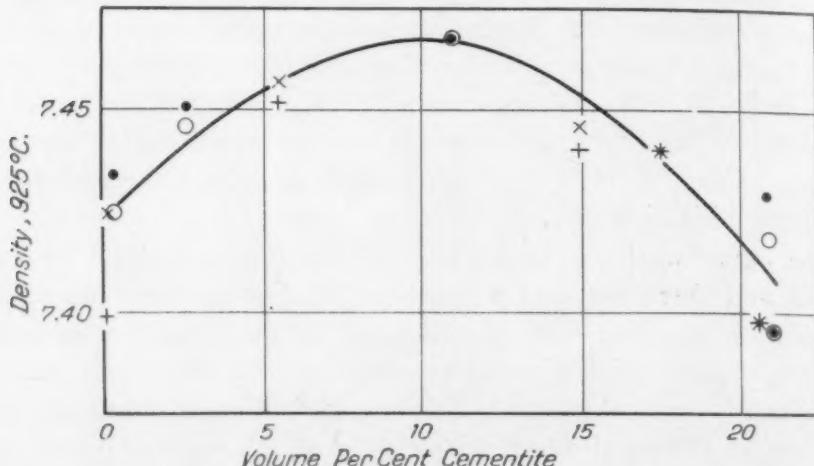


Fig. 4—Relation of Density at 925 Degrees Cent. (1700 Degrees Fahr.) to Volume Percentage of Cementite at Room Temperature of Metallic Matrix of Partially Graphitized White Cast Iron.

be determined as before by drawing a line tangent to the locus at the point under consideration and noting its intersection with the ordinates at zero and 100 per cent cementite.

Such a treatment shows that the density of cementite increases from about 6.7 when the temperature of 925 degrees Cent. (1700 degrees Fahr.) is first attained to about 8.2 when graphitization is nearly complete. Although not absolutely incredible within themselves, these figures are not in accord with the direct calculations from Fig. 1 which show that the density of cementite in the early stages of the reaction is probably not above 7.15 at 925 degrees Cent. (1700 degrees Fahr.) as shown in Table III. The solid solution density ranges from 7.6 in the beginning to 7.4 when graphitization is almost complete as against a value between 7.40 and 7.47 in Table III which may be considered fair agreement at least except for the values in the early stages of graphitization. If we combine the partial density of the two phases with their partial carbon content per unit

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volume, both derived as just indicated from Figs. 4 and 5, then we find that the carbon content of the cementite phase decreases from 11.3 to 3.9 per cent as graphitization goes on and that of the solid solution increases from about zero (or perhaps even a small negative value) to 1.08.

Now since no increment of carbon in the solid solution should occur during graphitization and since further no concentration of carbon below around 1 per cent seems possible, it is evident that the course of the curves in Figs. 4 and 5 is not that which would have

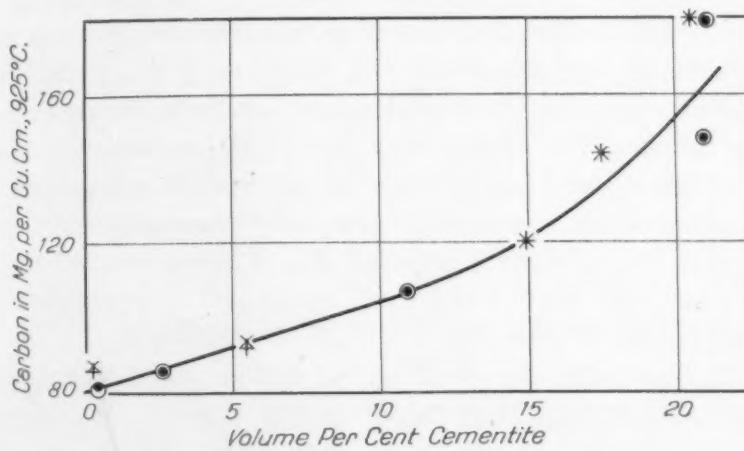


Fig. 5—Relation of Carbon Concentration Per Unit Volume at 925 Degrees Cent. (1700 Degrees Fahr.) to Volume Percentage of Cementite at Room Temperature of Metallic Matrix of Partially Graphitized White Cast Iron.

existed had we had the cementite volumes as they existed at 925 degrees Cent. (1700 degrees Fahr.). The consistency of results at least below 20 per cent cementite and of the data at 26 degrees Cent. makes one believe that the planimetric work is in fact reliable for the specimens as they exist in the samples when measured. It appears that a shift of the earlier cementite contents toward higher values might have yielded more nearly possible values whence one is led to suppose that the cementite occupies a relatively larger volume at high temperature than at room temperature, possibly with a corresponding change of carbon content. A comparison of Figs. 1 and 2 will show at once that alloys high in cementite contract more in passing from their state at 925 degrees Cent. (1700 degrees Fahr.) to that at which the specimens existed than do intermediate alloys but that the contraction for *very low* cementite alloys again increases. It is thought that these differences are in part due to changes in the

character of the cementite and reflect themselves as errors in evaluating the two figures last considered.

The density of cementite from Fig. 2, i.e., 7.335, is somewhat less than the accepted value. From the lattice parameter the density should be 7.84. There is thus reason to believe that the cementite in the "as is" condition is less dense than that upon which the reported spectrometric data of Wever were based. The density of cementite as arrived at from a study of the relation between carbon content and density of white cast iron is usually found at about 7.66.

In combining Figs. 4 and 5 to obtain a curve correlating density (hence specific volume) with agraphitic carbon content one would merely eliminate mathematically the work on volume percentage of cementite and get back to Fig. 1 which was constructed from the same original data for density and agraphitic carbon which were also used in Figs. 4 and 5 and which did not include any reference to volume percentage of cementite. One may then well ask for an explanation of the anomaly that from Fig. 1 we concluded that the cementite phase was  $Fe_3C$  and from Figs. 4 and 5 we conclude that the cementite phase is probably of variable composition.

The statement that the simplest, *but not the only*, interpretation of a straight line in Fig. 1 is that the system consists at all times of the same two components was advisedly made in anticipation of this contingency. An alternative assumption not inconsistent with Fig. 1 is that the cementite phase is not of constant composition (and density) but is continuously variable with the restriction that

$$\frac{1}{\rho} = 0.1324 + 0.0011 \times \text{Per Cent Carbon}$$

i.e., that the specific volume (or reciprocal of density) is by 0.0011 higher than 0.1324 for every per cent of carbon in the cementite phase. Mathematically the same conclusion holds for the austenite.

Metallurgically, there is no good explanation for postulating any changes of composition of the austenite but the reader needs not to be reminded that from the method of graphic solution by drawing tangents, one of the phases cannot be of variable composition unless the other is also.

Although we have in Fig. 3 some reasonably good suggestion that the cementite is actually  $Fe_3C$  in the tempered specimens, as one might expect, we lack any satisfactory basis for deciding directly or indirectly what rearrangements of volume and composition the so-

lution and carbide phases suffered during tempering. In interpreting Fig. 3 the reader may consider that the line marked "1 Per Cent Boydenite plus  $Fe_3C$ " represents also quite closely the conditions if the solid solution had been of metastable eutectoid composition at the moment of crossing the  $A_1$  line (8).

The data are neither sufficiently numerous nor sufficiently precise to warrant strictly quantitative conclusions. The following are offered as applying to the copper-bearing alloy investigated and probably also to the more usual white cast irons. During the process of graphitization at 925 degrees Cent. (1700 degrees Fahr.) the solid solution changes from one in equilibrium with cementite to one in equilibrium with graphite. The saturated metastable solution is higher than saturated stable solution. The changes in composition and density of austenite and cementite during graphitization have not been accurately followed because of the absence of quenched specimens. If there are progressive changes of composition they are restricted in such a manner that for both phases

$$(0.1324 + 0.0011 \times \text{Per Cent Carbon})_P = 1$$

at all times.

Specimens cooled quickly from 925 degrees Cent. (1700 degrees Fahr.) and subsequently tempered below  $A_1$  consist of  $Fe_3C$  and pearlite (granular) of eutectoid concentration. During tempering the carbide and (decomposed) solid solution phases experience changes of volume and probably of composition and density.

The transition from solid solutions of the austenite to those of the Boydenite type occurs fairly sharply at that agraphitic carbon content where cementite should vanish in view of the agraphitic carbon content of the alloy. In fact, however, some cementite survives this stage, representing the agraphitic carbon difference between saturated austenite and Boydenite and traces persist until stable equilibrium is reached. Very probably both systems coexist over an appreciable interval in the neighborhood of the transition point.

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## DISCUSSION

**Written Discussion:** By R. H. Harrington, research laboratories, General Electric Co., Schenectady, N. Y.

This paper indicates a very valuable continued interest of the authors in the subject of the possible "variable composition of cementite" in steels and cast irons.

The writer confesses that, after carefully reading the paper, his mind is a bit confused as to just what were the definite conclusions derived by the authors. For instance, the authors state (on page 559) that "we may be confronted with a mere inaccuracy of extrapolation, an effect of copper, an effect of subsequent heat treatment after quenching, or a decrease in cementite carbon content with progressing graphitization." The writer feels that scarcely one of these has been definitely proved or eliminated by the data presented. After all, this merely indicates the complexity and difficulty and intriguing appeal of this research.

There are some specific points to be noted:

1. No photomicrographs are shown to indicate the structures measured by the planimeter.
2. The etching reagent, used to develop such structure, is not indicated.
3. The magnification employed for measurement is not stated. If this was too low, there could result inaccurate measurements; if too high, sections might not be truly representative of such structures (as are shown by Smith and Palmer).
4. Could a copper-bearing precipitated phase (as shown in photomicrographs by Smith and Palmer, reference No. 4) cause difficulties in planimetric measurements or in density determinations?
5. In Fig. 1, from a purely statistical viewpoint, the data might well be considered insufficient to justify the representation by two straight lines rather than one.
6. The abstract fails to mention that a copper-bearing alloy was studied and hence implies that the statements made therein apply to an ordinary malleable iron. Smith and Palmer have shown that the copper affects the rate of graphitization and Sauveur states that copper tends to lower the critical points.

These facts might indicate also that copper very probably affects the composition of the phases involved.

7. There may be a matter of definitions involved. It might be well to define cementite as a compound containing 6.67 per cent carbon, for which there is considerable reason and substantiation. Granting this, the statement in the abstract that "the cementite decreases progressively in carbon content" could be changed. This may be more a matter of a non-equilibrium structure involving variable mixture of  $Fe_3C$  molecules and additional atoms of carbon or of iron, dependent upon reaction and diffusion rates, rather than a "phase" consisting of an established compound, but one of variable composition as seems to be implied at times.

One of the corollaries of the general theory of research into any one problem is that such research must inevitably lead to other intriguing and fundamental problems. It is to be hoped that the authors will continue this fine work which they have so well started.

#### Oral Discussion

L. L. WYMAN:<sup>1</sup> There is one point about the method of measurement to which I should like to call attention. In the paper the authors have used the planimetric method for the determination of carbide sizes, and in that connection, quite a number of years ago, in determination of particle size on very fine powders, it was found that by taking a micro-section of these powders mounted in a suitable medium and measuring the diameter visible in the microscope, the truth was not arrived at, and to get the truth of the matter it was found that a factor of 0.78 was necessary in determining the actual diameters of these particles. Thus, there is a possibility that unless the authors have taken this into consideration, they might have been 20 per cent in error in the original data which they obtained.

C. H. JUNGE: A full reply to the discussion will be in writing at a later date, but I can answer some of these questions now. In the first place, our density measurements on Fig. 1 were arrived at by computation from the initial specimens in the two series, so that all of our work on specific volume goes back to the density of specimens M-1 and M-6, with adjustment for the expansion up to 925, and to the expansion of 925 during the graphitizing reaction. Our measurements with the intercept planimeter were made on photomicrographs which were at 300 diameters. The original negatives were taken on 100 diameters on a specimen which had been etched in nitric acid, and then these negatives enlarged three times to give 300 diameter photograph to be used on an intercept diameter.

Unfortunately, these specimens were drawn at 650 degrees Fahr. which instead of giving a good dark troostitic matrix, which we would have preferred, there was a matrix which was more or less spheroidized, and hence, our determinations were perhaps not as accurate as they would have been if we had drawn them at a lower temperature in order to get a troostitic matrix.

#### Authors' Written Closure

Mr. Junge has already replied in part to certain features brought up by

<sup>1</sup>Research Metallurgist, General Electric Co., Schenectady, N. Y.

those who have kindly discussed this paper. In further reply to Mr. Wyman it may be said that we suppose from his rather brief statement that the problem represented the measurement of the diameter of the circular intercept of a sphere, the intercept being at a random distance from the center of the sphere and all of the sphere to be assumed to be of the same diameter. It is perhaps possible that Mr. Wyman's brief description has not given us a complete understanding of the point he is raising but admitting this to be

the case, the area of a semicircle is  $\frac{\pi r}{2}$ ; its total height at right angles to the plane of reference is  $r$ , therefore the mean value of the intercepted cord is  $\frac{\pi r}{2}$  which is  $\frac{\pi}{4}$  times the diameter of the circle ( $\frac{\pi}{4} = 0.78$ ).

It is to be noted that in Mr. Wyman's problem the question was to proceed from the average diameter of an intercept to an average diameter of a sphere; no similar problem can arise in the present case for the planimeter measuring simultaneously the areas of both phases, the sum unavoidably comes out 100 per cent. It seems impossible, therefore, to compare these conditions with those quoted by Mr. Wyman and his comment is believed to be interesting but inapplicable.

We have in the past repeatedly dealt with intercept planimeter work. It was described in some detail in replying to Dr. Harrington's discussion of the third reference of the present paper. Since our technique is substantially the same in all of our planimeter work, it appears that a reference to this earlier discussion is all that is necessary to supplement Mr. Junge's reply from the floor.

In the third reference we have also attempted to define what we believe to be a satisfactory use of the words cementite and iron carbide. It is definitely our opinion that the white homogeneous phase which the metallographer calls cementite is not of constant composition. The best interpretation of our entire investigation which we found it possible to make is contained in the last two paragraphs. Dr. Harrington's quotation from our page 559 is in reference only to the possible significance of a single one of our figures to which we were not able to assign one incontestable interpretation.

We do not happen to agree with Dr. Harrington that Fig. 1 admits of representation by a single straight line as plausibly as by the intercepting of two straight lines.

While it is true that we have not in the abstract mentioned the fact that our alloy contained copper, we trust that this has not been the occasion of much inconvenience for the second paragraph of our paper apprises the reader of that fact and the matter is again emphasized toward the close of the paper before presenting the conclusions.

If any existing iron-copper compounds change their density by heat treatment then we are not in a position to make suitable interpretations of the effect of such changes. It is our impression from Smith and Palmer's work here quoted that the lack of agreement between dilatometer readings and graphite content is not peculiar to copper-bearing alloys and therefore the effect cannot be ascribed primarily to the presence of copper compounds.

## ARC WELDING OF HIGH CARBON AND ALLOY STEELS

BY T. N. ARMSTRONG

### Abstract

*In welding high carbon and alloy steels by the arc process, the heat from the arc causes formation of a hardened zone in the base adjacent to the deposited metal. Unequal cooling strains set up in the deposit and the base cause cracks to occur in this heat affected zone. Heating the base prior to welding prevents welding cracks but pre-heating does not appear to improve bending properties of the weld, and apparently affects impact properties in the base metal and in the weld adversely.*

THE metallic arc process for welding metals has advanced rapidly during the past five years, due principally, to the development of electrode coatings that protect both the arc and the molten deposit from the atmosphere (1), (2), (3).<sup>1</sup> Deposits are obtained with the present covered electrodes that possess mechanical properties equal to or approaching the properties of the base (3), (4), (5). This development has resulted in a condition that is usually experienced with new materials and new methods, i.e., limits are placed on the application only after serious failures occur in service (6).

The arc welding process is applicable to most metals but the welding of steel is by far the most important. Satisfactory welds in low carbon, low alloy steels are dependent upon the skill of the operator (7), the condition of the equipment, the quality of the electrode and the welding sequence (8), but as the carbon and alloy content in steel increases, the metal in the base immediately adjacent to the deposit becomes harder. When a certain limit of carbon or alloy content is passed this area becomes quite brittle, and although the appearance of weld may be satisfactory, careful examination reveals small cracks in the zone adjacent to the deposit (9). In the manufacture of pressure vessels (10), (11), (12), weldments and cast-

<sup>1</sup>The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. The author, T. N. Armstrong, is assistant metallurgist at the Norfolk Navy Yard, Portsmouth, Va. Manuscript received May 27, 1935.

ings, it is the usual practice to subject the part to an annealing or stress relieving heat treatment after welding, but in structural welding it is usually impractical to attempt to subject the welds to heat treatment. Even though the part may be subjected to heat treatment subsequent to welding, heat treatment will not prevent welding cracks from occurring in high carbon and alloy steels.

### MATERIAL WELDED

It is difficult to attempt to definitely determine a limit of analyses beyond which cracks occur as there is a range of analyses in which welding cracks occur only at times. Steel containing not more than 0.30 per cent carbon, 0.70 per cent manganese, and no appreciable quantity of alloys will not crack on welding except under the most adverse conditions. To forestall criticism of selection of this limit, it is realized that steels containing appreciably more carbon or small percentages of alloys do not always crack, but as it cannot be anticipated with any degree of certainty that cracks will not occur, and as these cracks are not always easily discovered, such steels are not considered safe for welding.

Pieces from a steel rail containing 0.52 per cent carbon and 0.60 per cent manganese were machined to 6 by  $2\frac{7}{8}$  by  $1\frac{1}{8}$  inches. Pieces of a quenched and tempered plate containing 0.29 per cent carbon, 0.26 per cent manganese, 3.25 per cent nickel and 1.35 per cent chromium were machined to 6 by 6 by  $\frac{5}{8}$  inches. These two steels were selected to represent high carbon steel and alloy steel as it had been determined that steels of similar analyses could not be welded satisfactorily. Better comparison could have been made had the mass of the specimens been the same but as it was desired to make certain specific tests on the alloy plate, specimens from this material were cut to the desired size and specimens from the rail were made as large in cross section as the material available would permit. The alloy steel will be referred to as plate and the carbon steel as rail. The electrodes used were organic coated, mild steel, usually classed as heavily coated all position electrodes. As there are several establishments that manufacture this grade of welding rod the brand name is of no consequence.

### WELDING PROCEDURE

A single bead was welded in the center for the entire length of

each specimen. Beads were welded with  $\frac{1}{8}$ ,  $\frac{3}{16}$ , and  $\frac{5}{16}$  inch electrodes to determine the effect of electrode size, and with  $\frac{5}{32}$  inch electrodes on pieces heated to different temperatures to determine the effect of heating the base prior to welding (12). One section of plate was welded with two beads (Fig. 25) to determine the effect of the second or annealing bead on the affected zone in the base. The heated specimens were welded immediately upon removal from the furnace. Obviously there was some drop in temperature from the time the specimens were removed from the furnace to the time welding was completed, causing the true temperature to be less than the apparent temperature, however, the relation of the temperatures in the pieces during welding is believed to be the same as if no loss in temperature had occurred. After welding, sections were cut from each piece for microscopic examination and for hardness determinations (Figs. 1, 2, 3, etc.). In addition pieces were taken from the plate specimens for impact tests. Pieces for microscopic examination and hardness tests contained the bead, the heat affected zone, and a portion of the unaffected base. The beads on the impact specimens were ground flush with the top of the plate. Several bend test specimens were prepared by welding a piece of mild steel 3 by 2 by  $\frac{3}{8}$  inch to pieces of the plate 12 by 2 by  $\frac{1}{2}$  inch. The mild steel was welded along the edge by a double layer fillet on each side, across the center of the plate. The first layers were welded immediately after the alloy strips were removed from the furnace and the second beads were welded as soon as the slag was cleaned from the first beads, care being taken to prevent the second bead from touching the alloy plate. After welding, the mild steel combing was cut off just above the weld and the welded specimens machined to  $1\frac{3}{4}$  inch wide to remove the undercut at the ends of the beads. These pieces were bent by placing on supports 6 inches apart and applying the force through a 1-inch round bar laid immediately under the welded combing.

Pieces of both plate and rail were heated to 1600 degrees Fahr. (870 degrees Cent.) and quenched in water. These pieces were then tempered at the same temperatures as the preheating temperatures. The structure and hardness of these pieces were compared with those of the affected areas of the welded specimens.

#### HEAT AFFECTED ZONE

In steel welded by the arc process, there occurs in the base a

definite heat affected area, extending from the bottom of the deposit to the portion of the base in which the temperature is the temperature of the lower transformation point. This is the apparent affected zone and it is visible in all welded steel. The true affected zone extends beyond the apparent zone to that point in the base where the temperature does not affect the properties of the base. In annealed steels the apparent affected zone and the true affected zone are the same, but in quenched and tempered steels the true affected zone extends beyond the apparent affected zone to a point in the base where the temperature is the same as the original tempering temperature. If the base is cold at the time of welding and contains more than the safe limit of carbon and alloys, the apparent affected zone is composed principally of martensite. The metal in this area has been heated to above the critical range by the temperature of the arc and rapid cooling by conduction has an effect similar to that obtained by quenching. Cracks form in the apparent affected zone due to the inability of martensite to resist unequal cooling strains that occur in the deposit and in the base. If the base is heated prior to welding, the cooling rate in the affected zone is decreased, preventing or inhibiting martensite formation. Usually if martensite is not formed, welding cracks do not occur. In welds consisting of two beads, the apparent affected zone due to the last bead does not extend to the bottom of the first bead, however, the true affected zone extends beyond the initial bead into the base and usually, the temperature is sufficient to temper the martensite resulting from the first bead. But multiple layer welds do not prevent welding cracks as these cracks are caused by the first bead and the cracks usually have formed before the second bead can be deposited. Neither does heat treatment prevent cracks as the weld cannot be treated before the cracks occur.

The extent of heat affected zone is easily determined in the macrostructures but better comparison can be made by observing the values in Tables I and II. These data show that the depth of the heat affected area increases with the preheating temperature. The results due to electrode size are rather conflicting but it is logical to assume that the area increases as the electrode size increases as more heat is generated with the larger size rods. Rather surprising are the data showing that neither the electrode size nor the preheating temperature appears to have appreciable effect upon the penetration of the deposit.

Table I  
Weld Affected Area

Size Rod Dia. in Inches	Temperature of Base. Degrees Fahr.	Depth of Apparent Af- fected Area.		Penetration of Bead.	
		Rail	Plate	Rail	Plate
$\frac{1}{8}$	Approximately 35	0.0625	0.0781	0.0781	0.0625
$\frac{1}{8}$	Approximately 35	0.0781	0.0938	0.0625	0.0938
$\frac{1}{8}$	Approximately 35	0.0625	0.1094	0.0781	0.0781
$\frac{1}{8}$	200	0.0781	0.0938	0.0625	0.0626
$\frac{1}{8}$	400	0.0625	0.1094	0.0938	0.0781
$\frac{1}{8}$	500	0.0939	0.1250	0.0625	0.0781
$\frac{1}{8}$	700	0.1094	0.1406	0.0781	0.0781
$\frac{1}{8}$	1000	0.1719	0.2031	0.0625	0.0781
$\frac{1}{8}$	1250	0.2656	0.2813	0.1094	0.0781

Both steels cracked when welded cold or when welded at temperature below 500 degrees Fahr. (260 degrees Cent.). Cracks could not be detected in any piece that had been preheated to or above this temperature.

### HARDNESS OF THE WELD

There is no doubt that occurrence of cracks is directly related to hardness of the affected zone. Results in Table II show that hardness of this area decreases only slightly with increase in size of electrode but it decreases noticeably as the preheating temperature is increased. It is interesting to observe that the hardness of the bead is directly related to the hardness of the affected zone, although the increments are not so large because the range of hardness in the bead is confined to a much narrower range. In determining the hardness of the beads, readings were taken at the approxi-

Table II  
Hardness Data

Size Rod Dia. in Inches	Temper- ature of Base. Degrees Fahr.	Welded Rail		Brinell Hardness Welded Plate		Numbers Unaf- fected Zone		
		Bead	Hard- ened Zone	Unaf- fected Zone	Bead	Hard- ened Zone	Treated Zone	Treated Rail
$\frac{1}{8}$	35	235-256	470-511	181-208	278-282	423-446	231-235	( <sup>1</sup> )197 ( <sup>1</sup> )232
$\frac{1}{8}$	35	215-235	462-557	184-202	243-249	423-487	233-246	( <sup>2</sup> )640 514
$\frac{1}{8}$	35	199-208	385-426	177-187	249-280	420-466	245-251	...
$\frac{1}{8}$	200	243-246	365-487	182-191	280-288	398-446	227-235	( <sup>2</sup> )682 540
$\frac{1}{8}$	400	189-193	294-395	179-185	233-237	368-434	229-235	550 477
$\frac{1}{8}$	500	175-181	230-309	183-186	231-243	354-405	230-237	530 440
$\frac{1}{8}$	700	173-184	245-272	181-191	207-211	256-368	224-233	461 445
$\frac{1}{8}$	1000	146-162	197-229	181-186	187-198	245-339	227-238	321 302
$\frac{1}{8}$	1250	147-154	171-215	174-191	203-205	192-333	215-229	226 237
$\frac{1}{8}$ and $\frac{1}{8}$	35	.....	.....	156-190	-161	278-320	224-227	...

(<sup>1</sup>) Condition as received.

(<sup>2</sup>) Quenched from 1600 degrees Fahr. (870 degrees Cent.).

(<sup>3</sup>) Tempering temperature corresponds to preheating temperature.

mate center and near the fusion line. Almost without exception, readings taken near the fusion line were higher, indicating slight pick-up of base constituents by the deposit. The hardness of the apparent affected zone was greatest in the area slightly removed from the fusion line. This indicates that there is some impoverishment of base constituents where the base is in contact with the deposit. The hardness also dropped off from the maximum as the thermal critical line was approached. After crossing the thermal line the hardness was usually less than that of points in the unaffected base further removed from the weld. In two layer welds the hardness in the affected area of the first bead was greater than at any other place in the deposit. The area of the deposit beneath the first bead was softer than the second bead and the hardness in the affected zone of the base is considerably less than would have occurred had the deposit consisted of a single layer. Hardness values listed in Table II are the mean maximum and minimum obtained from the four to seven readings taken with a Vickers-Brinell machine.

#### STRUCTURE IN THE AFFECTED ZONE

Examination of the photomicrographs (Figs. 1 to 6) shows that the grains in the affected area adjacent to the deposit are extremely large. These large grains are the result of fusion of this area of the base by the heat from the arc. As the preheating temperature is increased, these grains appear to grow smaller, but examination at high magnifications shows that in reality the primary grains have not decreased in size, but with the change of constituents resulting from slower cooling rates, the structure appears to be fine-grained when viewed at low magnification. It is interesting to observe the difference in the microconstituents of the two metals in the affected zone (Figs. 7 to 12). This zone in the plate appears to be composed entirely of martensite after welding cold or if the preheating temperature has not reached 500 degrees Fahr. (260 degrees Cent.). At 500 degrees Fahr. (260 degrees Cent.) there appears to be some troostite although this constituent is not clearly resolved and with higher preheating temperature, even with considerable martensite present, this constituent appears to be more sorbitic than troostitic. With preheating temperature of 1250 degrees Fahr. (675 degrees Cent.) there appears to be some martensite formed. The rail, although containing some troostite in the affected zone when

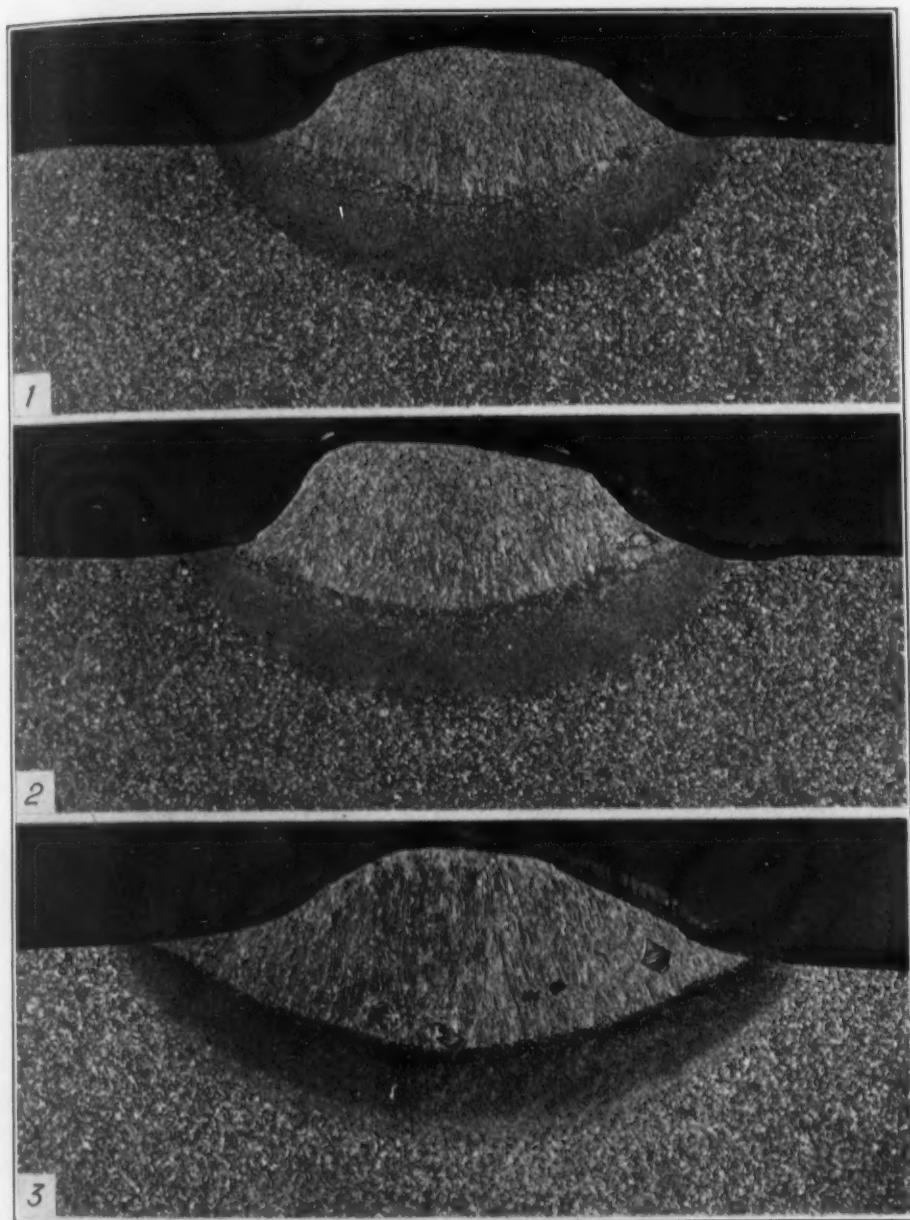


Fig. 1—Cold Rail Welded with  $\frac{1}{8}$ -Inch Rod.  $\times 5$ .  
Fig. 2—Cold Rail Welded with  $\frac{1}{16}$ -Inch Rod.  $\times 5$ .  
Fig. 3—Cold Rail Welded with  $\frac{1}{32}$ -Inch Rod.  $\times 5$ .

welded cold, possesses greater hardness than the plate. The quantity of troostite increases with the preheating temperature. At 500 degrees Fahr. (260 degrees Cent.) ferrite begins to precipitate out at the grain boundaries. At 700 degrees Fahr. (370 degrees Cent.)

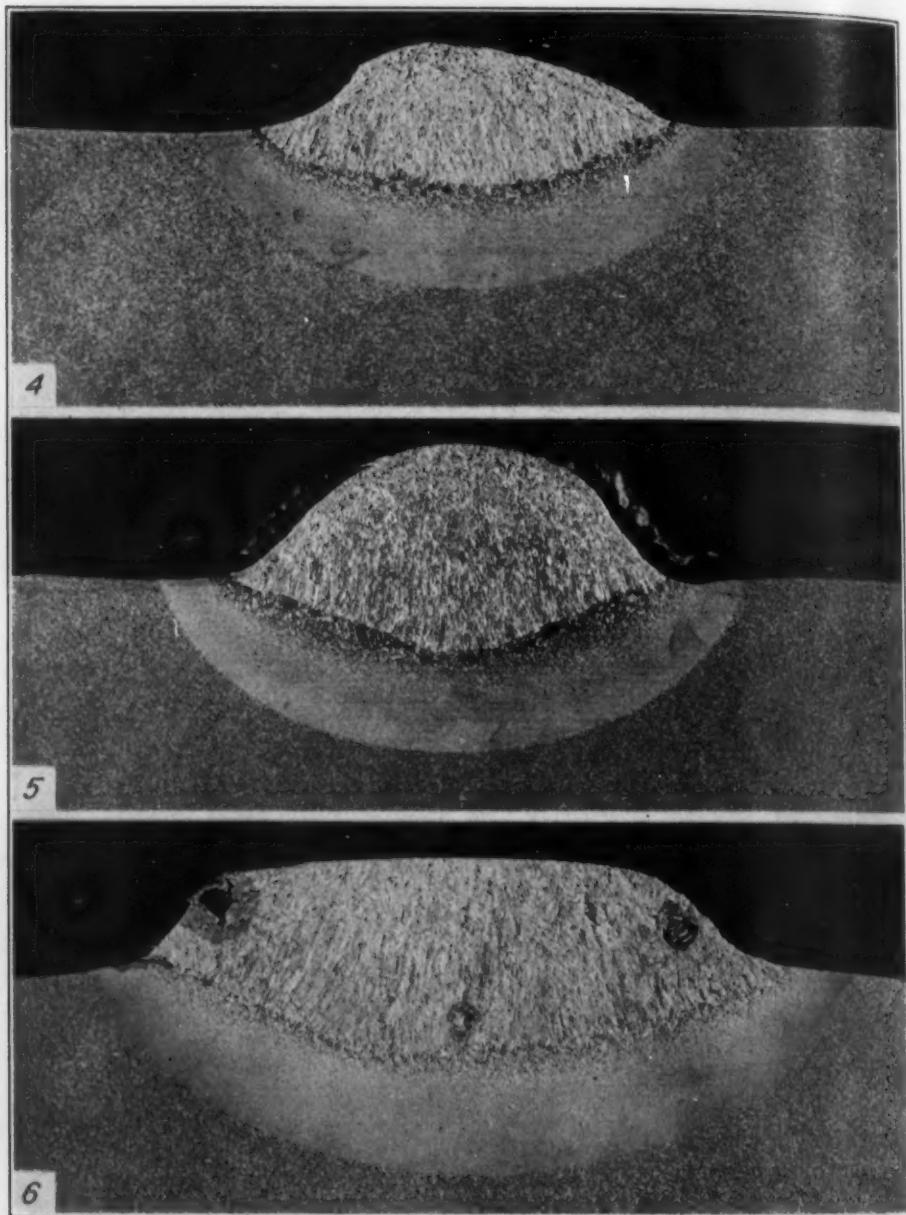


Fig. 4—Cold Plate Welded with  $\frac{3}{8}$ -Inch Rod.  $\times 5$ .  
Fig. 5—Cold Plate Welded with  $\frac{7}{16}$ -Inch Rod.  $\times 5$ .  
Fig. 6—Cold Plate Welded with  $\frac{1}{2}$ -Inch Rod.  $\times 5$ .

martensite has entirely disappeared and at 1250 degrees Fahr. (675 degrees Cent.) the structure is composed of ferrite, pearlite and troostite. In no instance is there evidence of sorbite in the welded rail.

The structure of the plate, in the as-received (Fig. 32) condi-

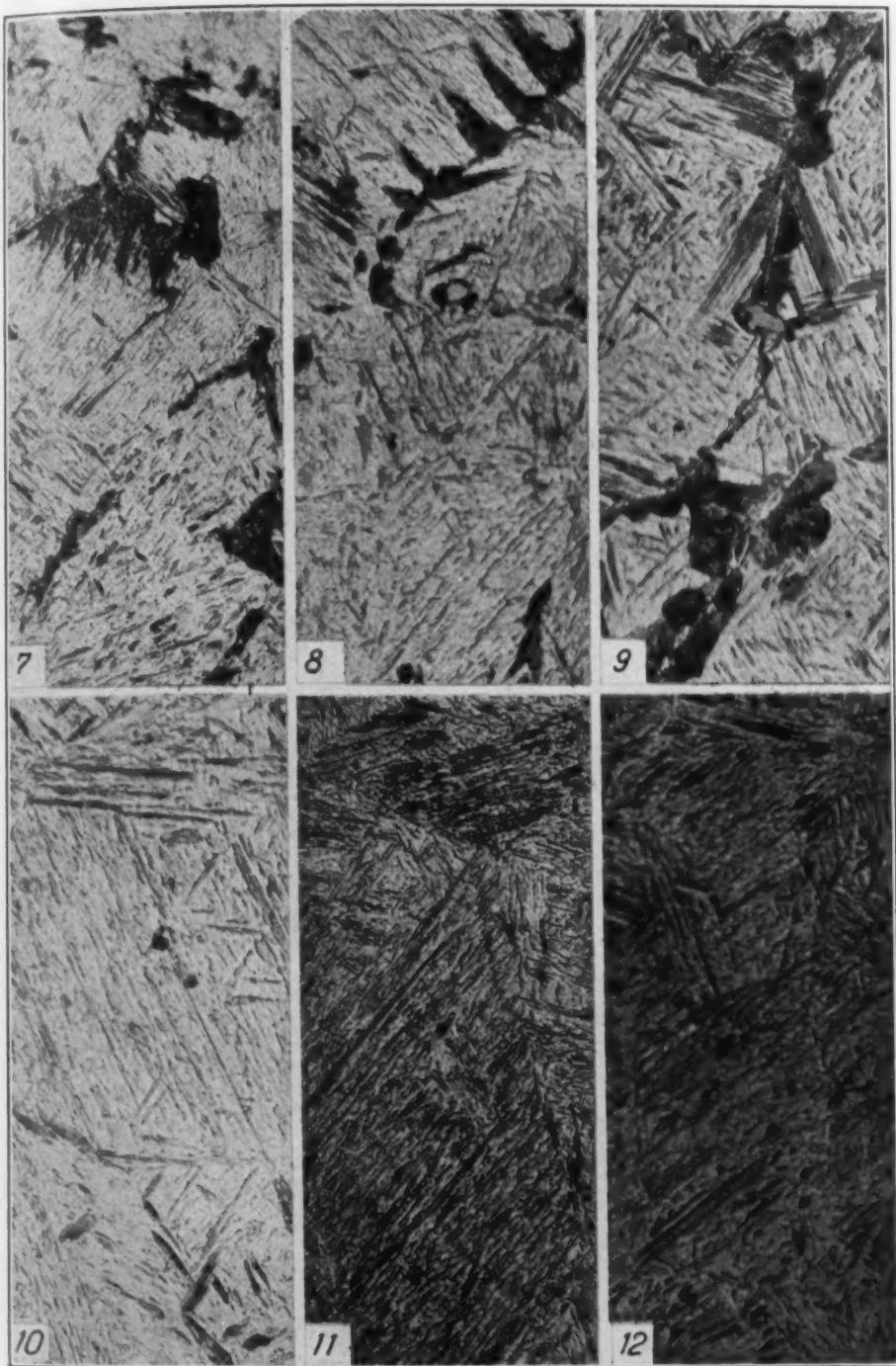


Fig. 7—Microstructure of Welded Rail in Affected Zone— $\frac{1}{16}$ -Inch Rod.  $\times$  500.  
Fig. 8—Microstructure of Welded Rail in Affected Zone— $\frac{1}{16}$ -Inch Rod.  $\times$  500.  
Fig. 9—Microstructure of Welded Rail in Affected Zone— $\frac{1}{16}$ -Inch Rod.  $\times$  500.  
Fig. 10—Microstructure of Welded Plate in Affected Zone— $\frac{1}{16}$ -Inch Rod.  $\times$  500.  
Fig. 11—Microstructure of Welded Plate in Affected Zone— $\frac{1}{16}$ -Inch Rod.  $\times$  500.  
Fig. 12—Microstructure of Welded Plate in Affected Zone— $\frac{1}{16}$ -Inch Rod.  $\times$  500.

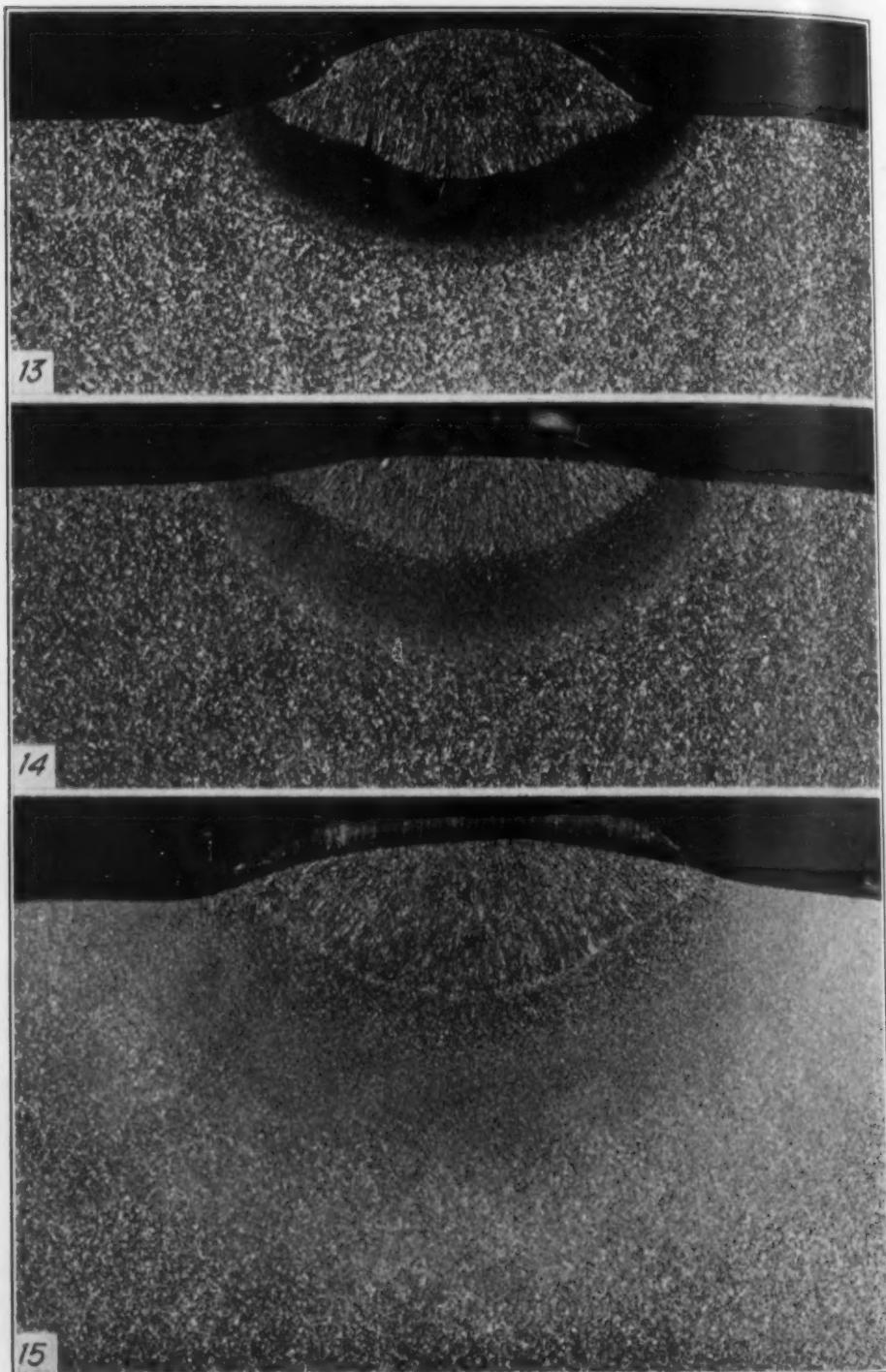


Fig. 13—Rail Preheated to 200 degrees Fahr. and Welded with  $\frac{1}{2}$ -Inch Rod.  $\times 5$ .  
Fig. 14—Rail Preheated to 700 degrees Fahr. and Welded with  $\frac{1}{2}$ -Inch Rod.  $\times 5$ .  
Fig. 15—Rail Preheated to 1250 degrees Fahr. and Welded with  $\frac{1}{2}$ -Inch Rod.  $\times 5$ .

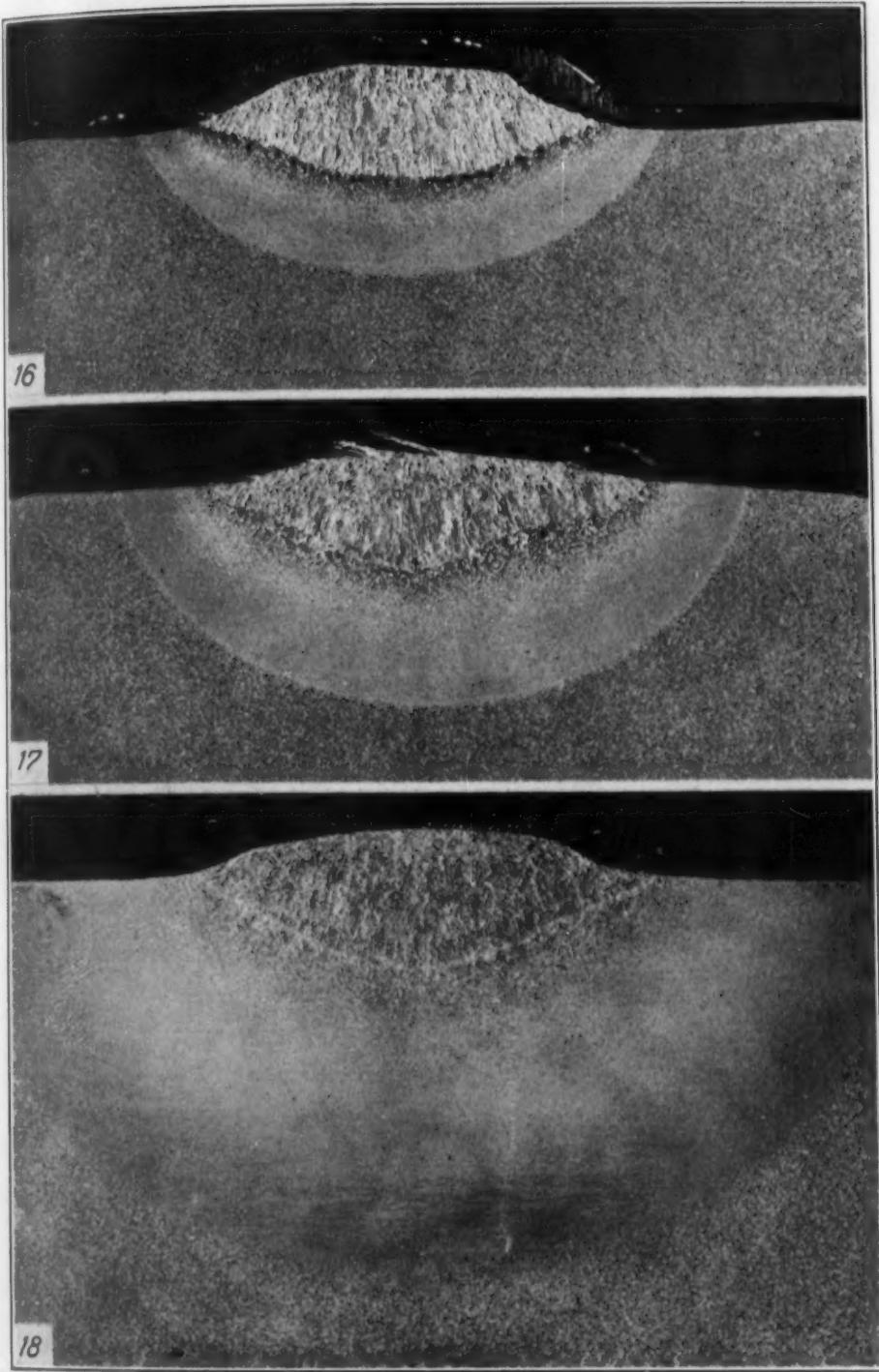


Fig. 16—Plate Preheated to 200 degrees Fahr. and Welded with  $\frac{1}{8}$ -Inch Rod.  $\times$  5.  
Fig. 17—Plate Preheated to 700 degrees Fahr. and Welded with  $\frac{1}{8}$ -Inch Rod.  $\times$  5.  
Fig. 18—Plate Preheated to 1250 degrees Fahr. and Welded with  $\frac{1}{8}$ -Inch Rod.  $\times$  5.

$\times$  5.  
 $\times$  5.  
 $\times$  5.

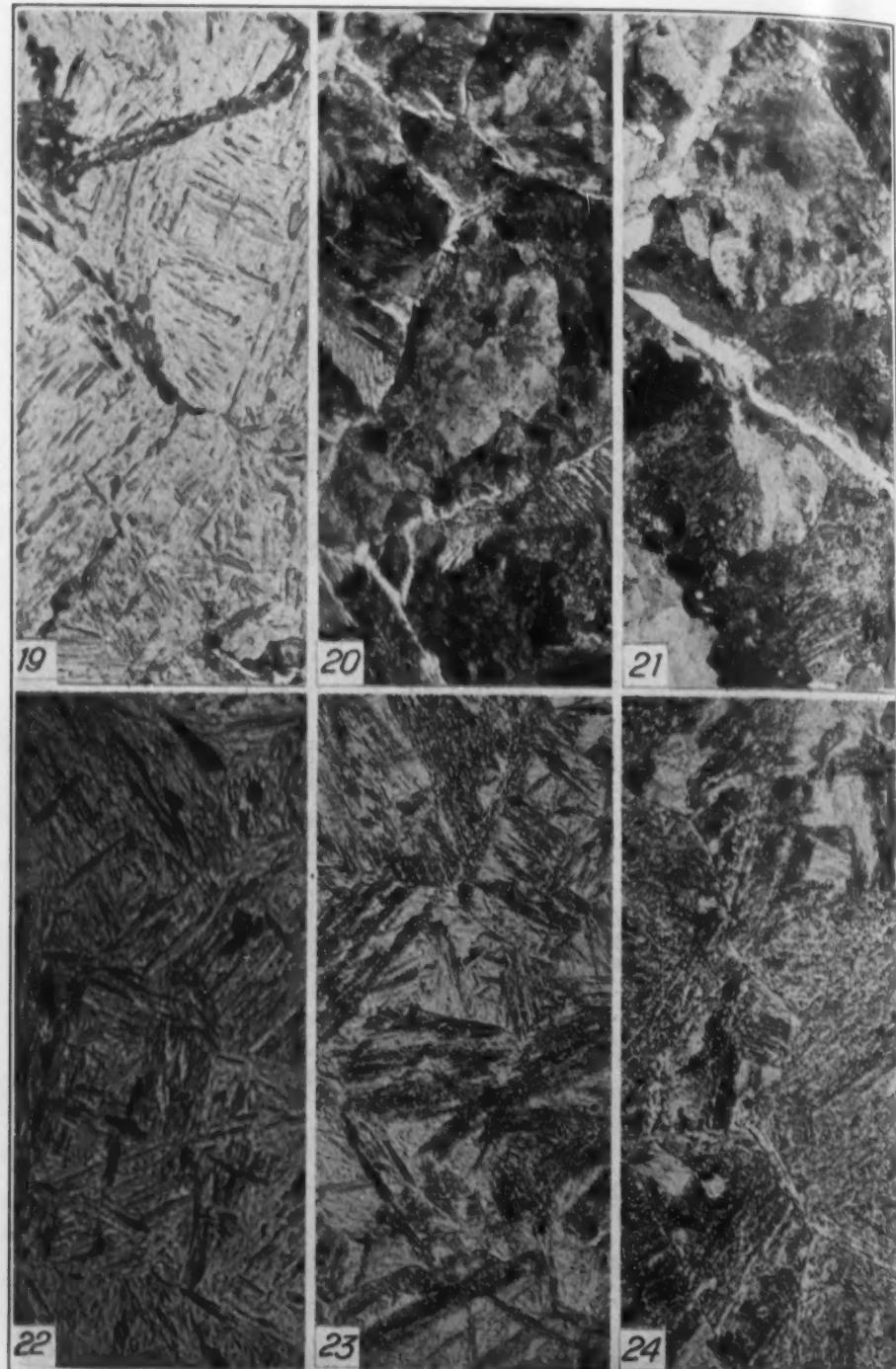


Fig. 19—Rail in Affected Zone Preheated to 200 Degrees Fahr. and Welded.  
Fig. 20—Rail in Affected Zone Preheated to 700 Degrees Fahr. and Welded.  
Fig. 21—Rail in Affected Zone Preheated to 1250 Degrees Fahr. and Welded.  
Fig. 22—Plate in Affected Zone Preheated to 200 Degrees Fahr. and Welded.  
Fig. 23—Plate in Affected Zone Preheated to 700 Degrees Fahr. and Welded.  
Fig. 24—Plate in Affected Zone Preheated to 1250 Degrees Fahr. and Welded.  
All Welds Made with  $\frac{1}{2}$ -Inch Rod. All Photomicrographs  $\times 500$ .

tion, was composed of very fine sorbite that could not be completely resolved by the microscope. This steel had previously been treated by quenching from above the critical and tempering at 900 degrees Fahr. (480 degrees Cent.). The structure of the rail (Fig. 29) was coarse-grained and consisted of free ferrite and pearlite. Structures resulting from quenching the pieces from 1600 degrees Fahr. (870 degrees Cent.) and tempering at the same temperatures as the pre-heating temperatures were quite different from the structures in the affected zone of the welded pieces. The quenched plate contained only martensite but it was finer grained than the martensite in the pieces welded cold. The quenched rail contained both martensite and troostite but apparently more martensite than the welded piece. Martensite appeared to be entirely broken down in both steels by tempering temperatures above 400 degrees Fahr. (200 degrees Cent.). At 1250 degrees Fahr. (675 degrees Cent.) both steels are entirely sorbitic. It is quite interesting to observe that the troostite formed in the rail on welding is quite different in appearance from the troostite formed by quenching and tempering.

#### EFFECT OF PREHEATING ON IMPACT VALUES

The impact values, Table III, both in the weld and in the area away from the weld decreased appreciably when the preheating temperature exceeded 200 degrees Fahr. (100 degrees Cent.), but ap-

Table III  
Izod Impact Results on Alloy Steel Plate

Size Rod Dia. in Inches	Temp. of Plate Deg. Fahr.	Notched Across Weld Ft.-Lbs.	(1) Notched at Weld Ft.-Lbs.	(2) Notched in Plate	(3) Notched in Plate
$\frac{1}{8}$	35	43.0	33.0	61.0	52.0
$\frac{1}{8}$	35	39.0	40.0	60.0	51.0
$\frac{1}{8}$	35	31.5	52.0	58.0	50.0
$\frac{1}{8}$	200	35.0	35.0	59.0	53.0
$\frac{1}{8}$	400	27.0	...	31.0	29.0
$\frac{1}{8}$	500	23.0	...	32.0	28.0
$\frac{1}{8}$	700	25.0	...	33.5	29.0
$\frac{1}{8}$	1000	23.0	...	36.0	30.0
$\frac{1}{2}$	1250	21.0	...	35.5	31.0

(1) Notched on opposite side from weld immediately below weld.

(2) Notched in plate same side as weld but in unaffected area below weld.

(3) Notched in plate side 90 degrees from weld in unaffected area above weld.

parently preheating to 1250 degrees Fahr. (675 degrees Cent.) had no more effect than heating to 400 degrees Fahr. (200 degrees Cent.). The writer is at a loss to explain why the impact values fall off so

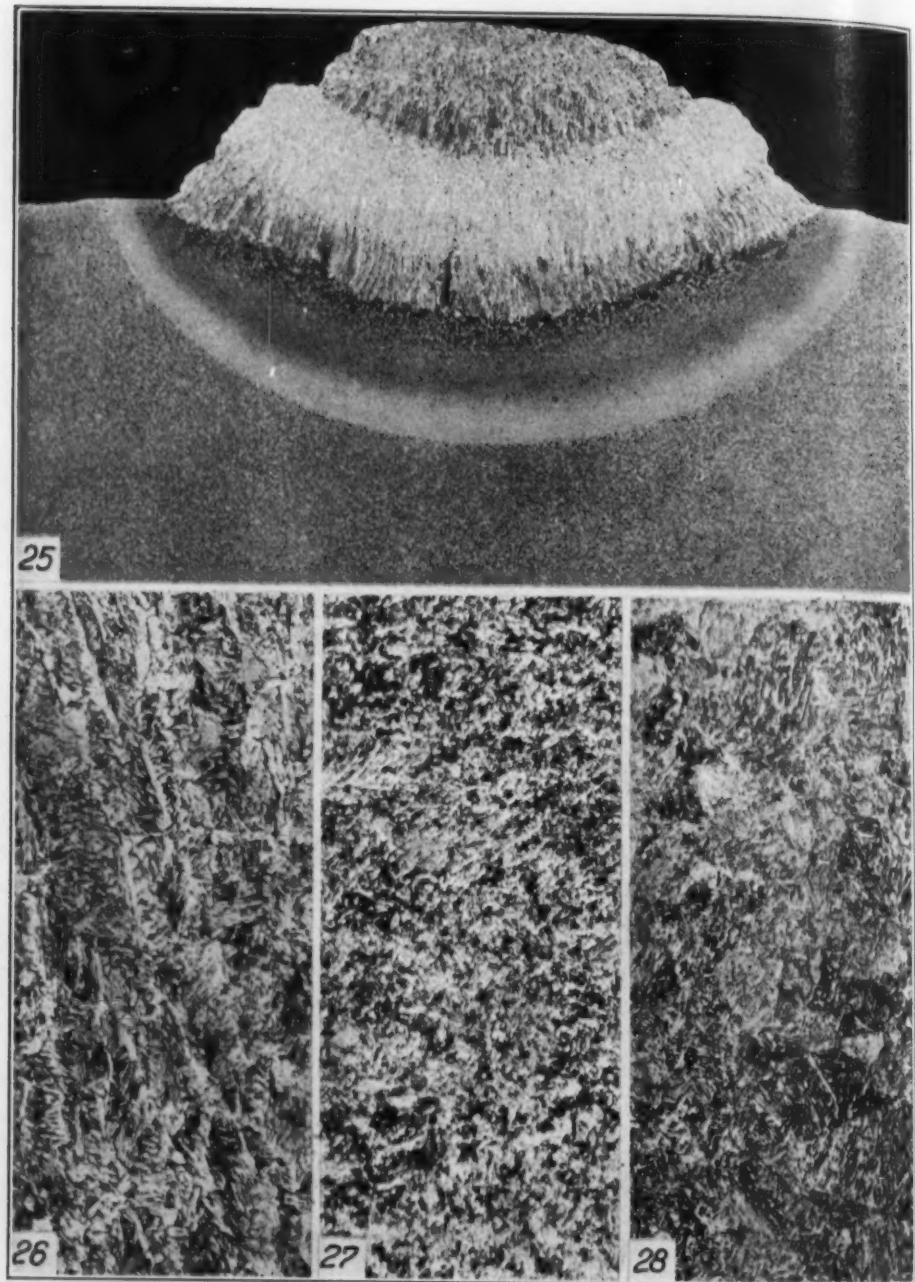


Fig. 25—Cold Plate Welded with  $\frac{1}{4}$ -Inch and  $\frac{1}{2}$ -Inch Rod—Two Beads.  $\times 5$ .

Fig. 26—Microstructure in Top of Bead of Plate Welded with Two Beads.  $\times 100$ .

Fig. 27—Microstructure in Affected Zone of Bottom Bead of Plate Welded with Two Beads.  $\times 100$ .

Fig. 28—Microstructure in Affected Zone of Plate Welded with Two Beads.  $\times 100$ .

greatly, particularly in the unaffected area, when preheating was conducted at temperatures considerably lower than the original tem-

pering temperature of the plate. The impact values at the welds were considerably less than in the unaffected area. At the welds, impact values decreased as the preheating temperature increased. Whether the specimen was notched in the weld or on the side opposite to the weld did not appear to affect the results appreciably. When notched on the welded side it was necessary to grind the notches in as the metal was too hard to attempt to machine.

#### EFFECT OF WELDING ON BENDING PROPERTIES

A piece of plate of 1 by  $\frac{1}{2}$  inch section was bent to 180 degrees around 1-inch diameter prior to welding. A similar specimen that had had a bead welded across the top, bent to 15 degrees. By heating the specimen prior to welding the angle of bend was increased to as much as 60 degrees. These results indicate that preheating improves the bending properties but results of bending the pieces with the weld attached mild steel combing show conclusively that preheating does not improve the bending properties of this type of weld. Welding cracks were prevented in these pieces by preheating the plate and as each specimen was welded with double layer welds, it was anticipated that there would be no martensite present, however, on machining these specimens after welding it was necessary to grind the welds on specimens that had been preheated below 1000 degrees Fahr. (540 degrees Cent.). This indicates that the heat from the second bead is not always sufficient to temper the affected zone in the base.

In attempting to develop a method of welding wrought high carbon and alloy steels by first preheating the base, it was realized that preheating temperature would have to be limited to the tempering temperature of quenched and tempered steels. It was also realized that distortion would increase with the preheating temperature. Such success had been experienced with the preheating method for welding hard steel castings that it appeared to be quite simple to extend the method to wrought steels. It was most surprising to find that instead of being beneficial, other than preventing welding cracks, preheating not only affected the properties of the weld adversely but appeared to embrittle the steel in areas that were unaffected by the weld. In the final analyses proof of any weld is the manner in which it acts under service conditions. The specimens prepared by welding a piece of mild steel to the plate assimilate a very

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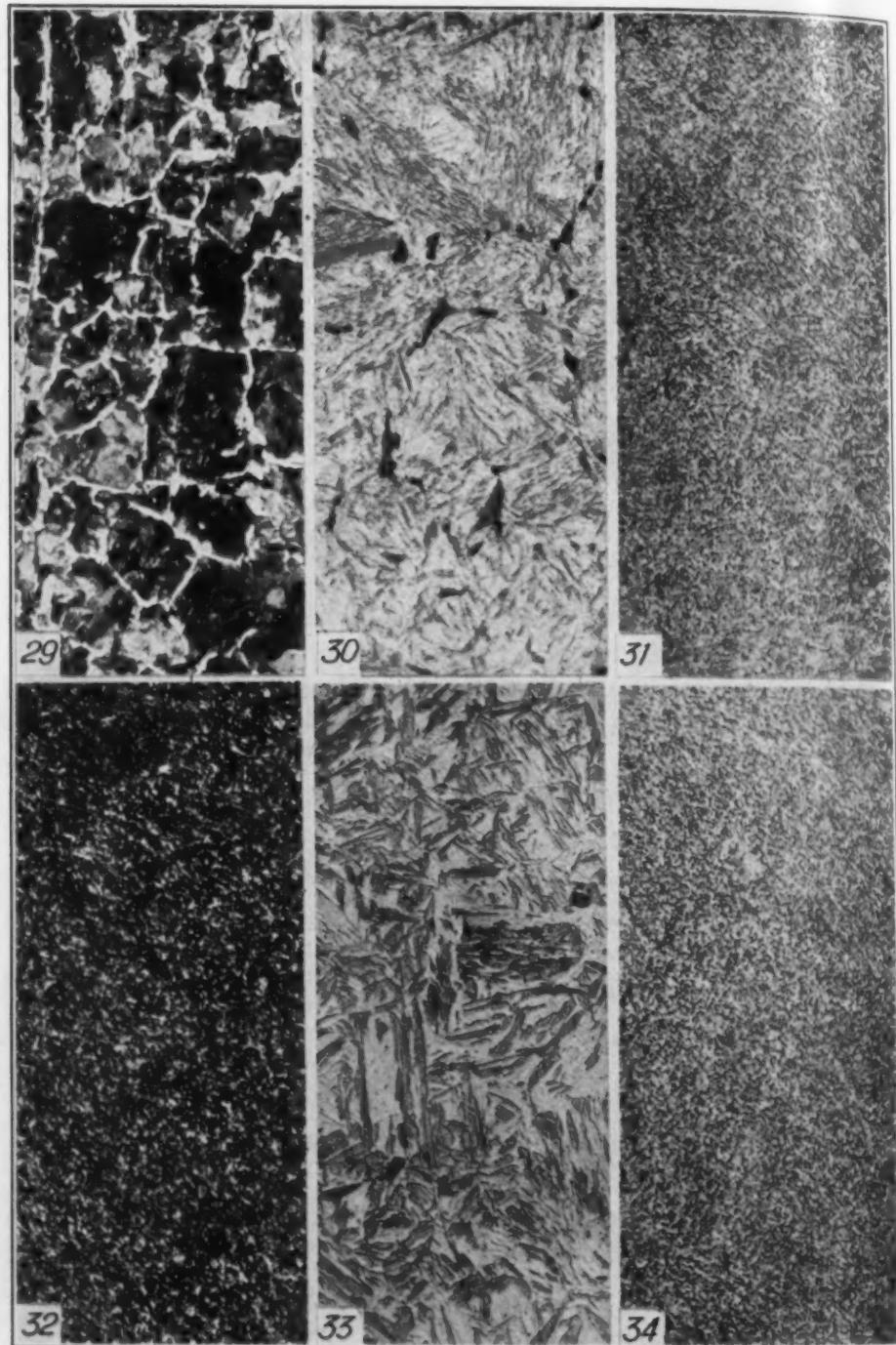


Fig. 29—Microstructure of Rail As-Received.  $\times 100$ .  
Fig. 30—Microstructure of Rail Quenched at 1600 Degrees Fahr. Not Tempered.  $\times 100$ .  
Fig. 31—Microstructure of Rail Quenched at 1600 Degrees Fahr. Tempered 1250 Degrees Fahr.  $\times 100$ .  
Fig. 32—Microstructure of Plate As-Received.  $\times 100$ .  
Fig. 33—Microstructure of Plate Quenched at 1600 Degrees Fahr. Not Tempered.  $\times 500$ .  
Fig. 34—Microstructure of Plate Quenched at 1600 Degrees Fahr. Tempered 1250 Degrees Fahr.  $\times 500$ .

popular type of welded joint. It is admitted that the method of testing these specimens is rather severe yet results indicate what may be expected of the welded structure. Also, steel that is safe for welding, when subjected to this test, gives very satisfactory results. This same type of specimen has been made of rolled steel containing considerably less carbon than the rail, and on rolled alloy plate that contained considerably less alloy than the above plate, and the alloys other than nickel and chromium. These steels contained more carbon or more alloy than was considered safe for welding. Results of these tests were similar to the results obtained with the treated nickel-chromium steel plate. All of these results indicate that welding of high carbon and alloy steels is, at best, not satisfactory if the steel is to be used in structural members.

### CONCLUSION

This investigation has resulted in the collection of considerable data, most of which are negative; however, it is believed that these data add to the present knowledge of the arc welding process, and indicate the necessity of limiting arc welding to the softer steels. No matter what type of electrode is used, brittleness will occur in the heat affected zone of the base metal if the carbon or alloy content in the base is above the limit safe for welding. The properties of the deposit may be controlled by electrode composition but brittleness in the affected zone of the base is controlled by heat (cooling rate) and by the chemical composition. It appears that future efforts will have to be directed toward development of alloy steels that will be free from martensite in the affected zone on welding. Some progress has already been made in this direction, as several manufacturers are now offering low alloy steels of low carbon content, but the strength of these steels is somewhat limited (13), (14), (15). It is probable that the answer will be found, not by limiting the carbon but by proper alloy combination. If air hardening of chromium steels can be controlled by titanium additions (16), it appears that titanium may prove to be the controlling factor in welding hard steels successfully.

### ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of J. A. Duma,

junior metallurgist at the Norfolk Navy Yard, for collection of data and for the photomicrographs.

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### DISCUSSION

**Written Discussion:** By P. E. McKinney, Bethlehem Steel Co., Bethlehem, Pa.

The author has presented a very interesting and complete analysis of the characteristics of electric welds made on air-hardening steel, using one method of welding which is fully described. The methods of test used for demonstrating the characteristics of parent metal, weld metal and affected zone, have been well selected to present data that is readily interpreted. Such methods of

examination of cross sections of welds or of weld beads are quite reliable for the study of influence of welds on surrounding metal.

The general question of weldability of high carbon and alloy steels is one on which considerable difference of opinion has been expressed. Weldability in its broadest sense covers a very wide field and it is unsafe to class any material as definitely weldable or unweldable without some consideration of the service applications which are contemplated for the welded parts. Even in the case of high carbon and alloy steels which are very definitely air hardening, welding is entirely safe and practical for building up hard wearing surfaces in some parts of equipment which are not subject to severe service stresses which would be influenced by the affected underlying zone. It is quite obvious, however, that where such a disturbance occurs in all of the physical characteristics of the material surrounding the weld as is shown by the author in these instances, any application of the welded part to service where these characteristics are essential, is to say the least, a hazardous undertaking.

The data presented by the author shows rather conclusively the danger of attempting to weld quenched and tempered or specially heat treated material without a very thorough study of the effect of such welding operations on the metal surrounding the weld.

It may be contended that with proper stress relief or heat treatment after welding these ill effects can be corrected. This is hardly true as stress relieving at temperatures below the critical range, while very effective in relieving mechanical strains, will not correct the disturbances in structural characteristics such as shown by the author on these samples of air hardening steel.

The results shown in Table III of the author's paper on the effect of pre-heating temperature on impact properties of the alloy steel plate material, are very interesting but are not at all surprising. While the identity and heat treatment of the plate material used in these tests is not given, the characteristics as shown in the test data indicate that the original plate was of material specially heat treated to resist impact of high magnitude. The heat treatment given to some of these materials is of a very special character to develop these extraordinarily high impact values and any disturbance of the material by re-heating will usually change these values very materially. While temperatures as low as 400 degrees Fahr. do not usually affect the material, any temperatures such as are ordinarily used for preheating in welding, will most certainly adversely affect impact values.

In the author's work the welding was performed with covered mild steel electrodes, therefore, the results reported are not necessarily comparable with those which might be obtained with modifications of this practice. In welding air hardening steels the use of other types of electrodes is often resorted to. Such materials as the austenitic chromium-nickel steels which require very much lower amperage for satisfactory fusion and penetration, are often used so as to avoid the development of severe hardening under the weld. Some of the newer types of electrodes in which part of the alloying materials have been incorporated in the coating, have also been found better than standard electrodes for certain applications.

If this same material were tested using variations in technique involving the use of other electrodes, it is highly probable that different results than

those reported by the author would be obtained but it is reasonably certain that in the welding of material of this character no modifications in welding technique would produce results showing a lack of serious disturbance of the metal underlying or surrounding the weld. Certainly no assumption should be made that this type of material could be welded without such effect until tests similar to those made by the author had demonstrated these facts beyond a doubt.

There appears to be a wide field for further investigation in the development of high strength alloy steels which are capable of being welded without the development of a hard brittle zone surrounding the weld and at the same time capable of developing the physical properties desired in service. Further investigation may indicate that certain stabilizing additions may be beneficial but this certainly has not been proven up to the present time.

It appears that this subject is one which merits the close attention of all our technical societies interested in the metallurgical and welding characteristics of alloy steel.

#### Oral Discussion

L. C. BIBBER:<sup>1</sup> I would like to explain the use of bend testing in determining the effect of welding on hardenable steels. Fig. A shows the hardness of ordinary mild steel base metal when welded with a double headed fillet weld. The maximum hardness changed from 150 to 217 Vickers. We explored the

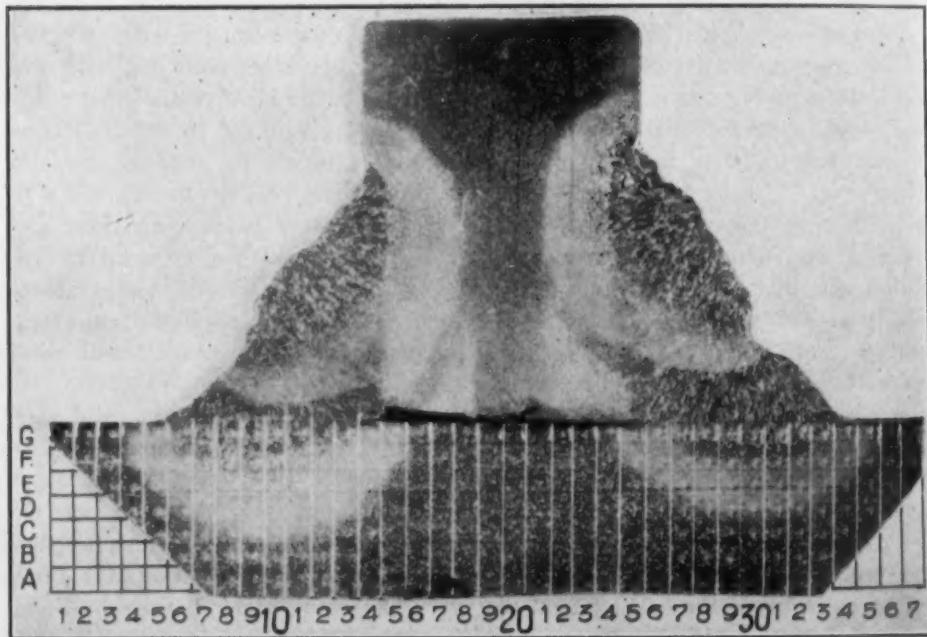


Fig. A—Effect of Welding on Hardness of Mild Steel Base Metal (0.31% C). Vickers Hardness Numbers Shown in Following Tabulation.

<sup>1</sup>Formerly Senior Welding Engineer, Bureau of Construction and Repair, U. S. Navy Dept., Washington, D. C. At present associated with Carnegie-Illinois Steel Corp., Pittsburgh.

A		B		C		D		E		F		G	
1	2											136	
3	4											136	
5	6											145	
7	7	147	147	147	148	148	148	150	150	150	147	147	
8	9	150	152	151	152	151	152	150	155	157	155	167	165
10	11	148	147	147	148	147	147	145	160	163	184	198	165
11	12	145	147	147	148	148	148	147	158	160	180	206	165
12	13	147	147	147	147	147	147	145	155	158	179	217	165
14	15	155	155	155	155	155	155	155	155	155	169	180	160
16	17	156	156	156	156	156	156	156	156	156	150	140	114
18	19	119	119	119	119	119	119	119	119	119	180	180	114
20	21	121	121	121	121	121	121	121	121	121	180	180	114
22	23	222	222	222	222	222	222	222	222	222	180	180	114
24	25	123	123	123	123	123	123	123	123	123	180	180	114
26	27	156	156	156	156	156	156	156	156	156	163	163	147
28	29	154	154	154	154	154	154	154	154	154	167	167	147
30	31	154	154	154	154	154	154	154	154	154	155	155	147
32	33	156	156	156	156	156	156	156	156	156	171	171	147
33	34	156	156	156	156	156	156	156	156	156	164	164	147
34	35	158	158	158	158	158	158	158	158	158	163	163	147
36	37	156	156	156	156	156	156	156	156	156	160	160	147

## VICKERS HARDNESS NUMBERS

entire area, as can be seen from the Vickers impressions on the accompanying macrograph, Fig. A, as well as on the coordinate hardness chart above.

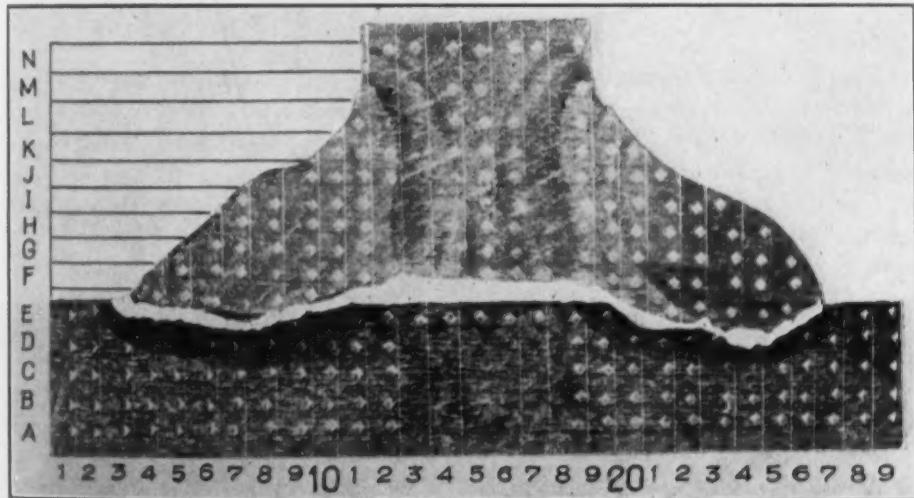


Fig. B—Effect of Welding on Hardness of High Carbon Steel Base Metal (0.45% C). Vickers Hardness Numbers Shown in Following Tabulation.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	Row	Column
168	173	174	188	197												1	1
171	181	184	188	197												2	2
176	183	184	193	174												3	3
179	187	190	505													4	4
177	189	199	517													5	5
181	190	192	361													6	6
178	191	202	269													7	7
184	190	201	308													8	8
182	192	191	315													9	9
177	190	189	226	314												10	10
173	181	190	194	250												11	11
172	172	187	198	216												12	12
				208												13	13
				198												14	14
				191												15	15
				191												16	16
				191												17	17
				202												18	18
				181	187	211	217		195	213	201	195	197	188	191	187	187
				174	183	191	207	309		202	193	189	186	186	184	168	19
				177	183	188	307			187	186	179	174	174	167		20
				176	185	200	272		168	209	184	182	197	191		21	
				180	188	206	322			224	226	199	218	228		22	
				184	193	258	176			223	209	217	231	214		23	
				185	199	252				248	205	228		232		24	
				185	199	216				247	201			216		25	
				188	197	209					307					26	
				187	197	204						362				27	
				188	196	200						202				28	
				186	189	194						198	197			29	

### VICKERS HARDNESS NUMBERS

Fig. B shows a corresponding chart of a 0.45 per cent carbon steel forging. In this instance, when the welds were applied the standing member broke off. It will be noted that the maximum hardness was 517 Vickers, attained by merely welding on a 0.45 per cent carbon steel forging.

Fig. C shows the macro and micro study of that steel. In the hardened zone underneath the welding will be noted cracks which extended down into the base metal. These can be seen in the other views as well as the martensitic structure to the left.

In some of our early work tensile investigations of the effect of depositing weld metal on high tensile steel were made. In many instances, it was noted that failure occurred in the base metal immediately outside of the weld as can be seen in Fig. D. This led to the belief that there was a weakness on the tension side.

We then made tee-bend specimens and bent them as shown in Fig. E. Failure occurred in the base metal alongside the weld. This is not a test of weld metal, it is a test of the base metal. The failure is often manifested

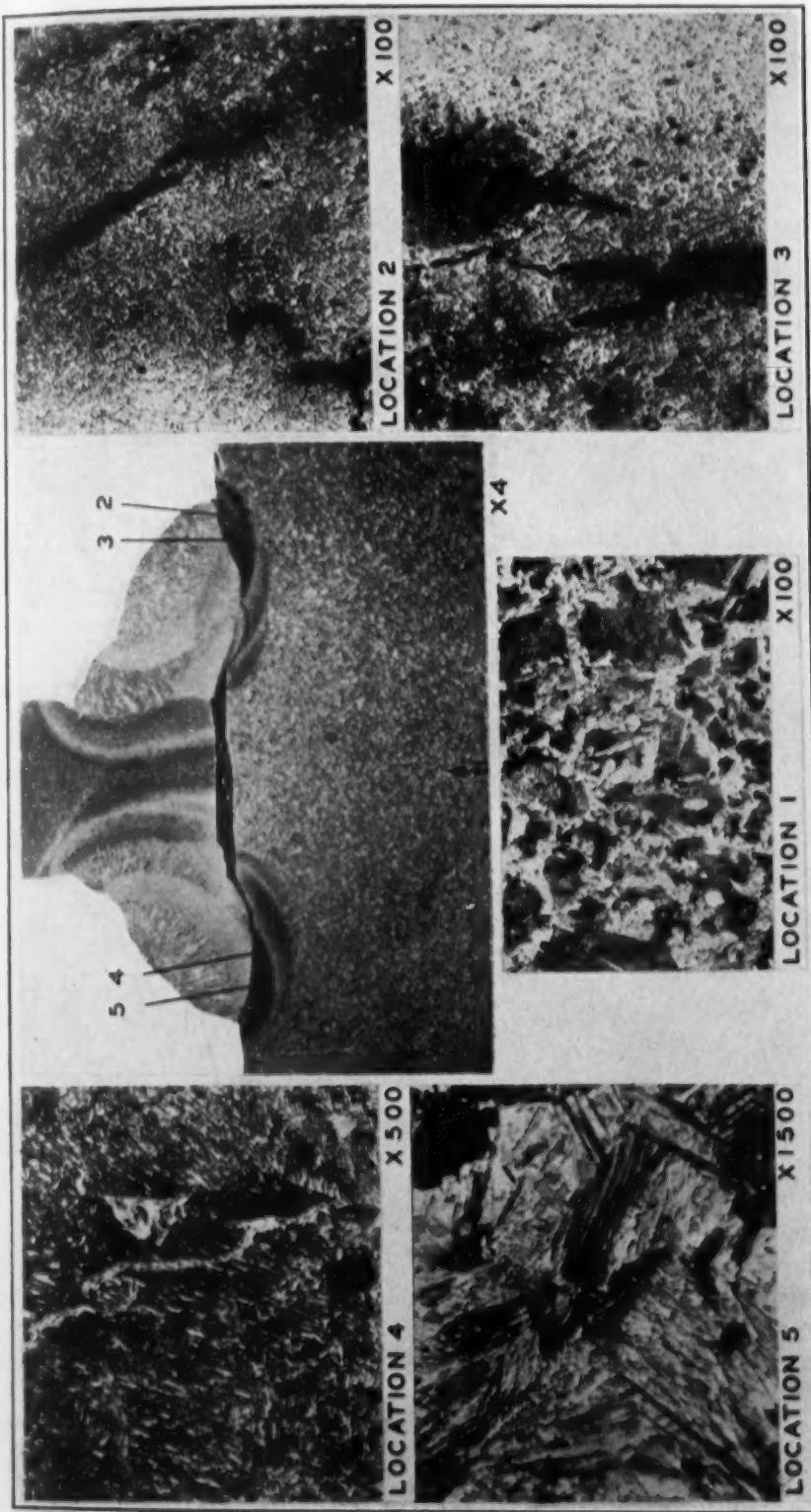


Fig. C—Showing Macro and Micro Study of 0.45% C Steel Forging Welded.

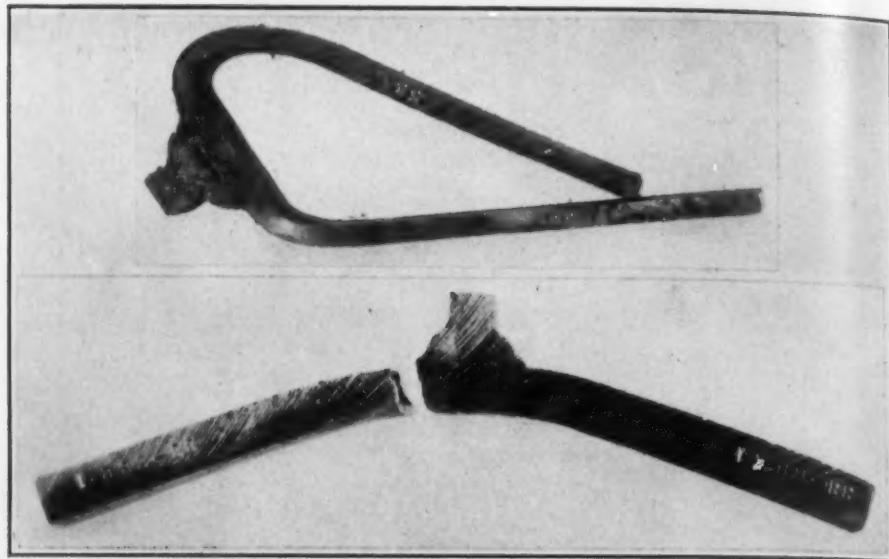


Fig. D—Effect of Thickness on Bending of Silico-Manganese Steel. Angle of Bend of Upper Piece 90 Degrees Without Failure.  $\frac{3}{4}$ -Inch Stock. Angle of Bend of Lower Piece 21 Degrees.  $\frac{1}{2}$ -Inch Stock.

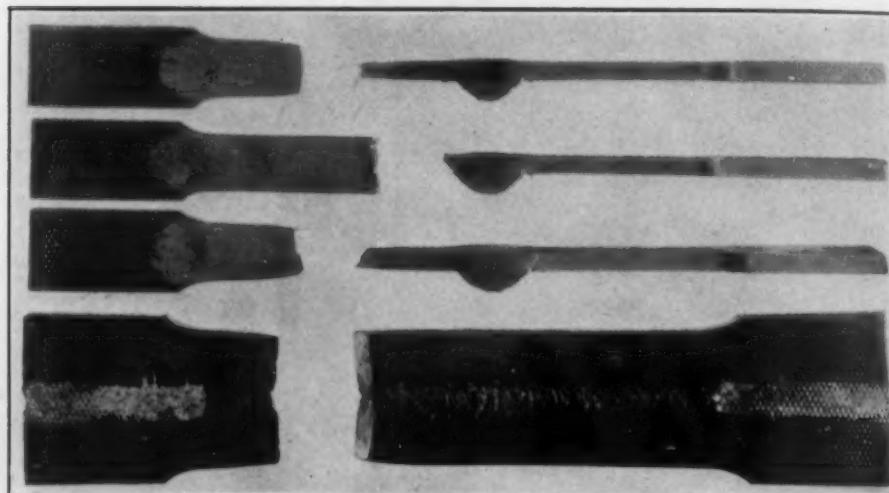


Fig. E—Effect of Welding on Tensile Specimens.

in a sharp crack or break. If the material is thin it can be bent readily. The two steels in Fig. E are of the same composition; one is  $\frac{1}{2}$  inch thick and the other  $\frac{1}{9}$  inch thick. For structural work a thickness of  $\frac{1}{2}$  inch is most often used as a means of determining the satisfactoriness of hardenable steel for welding.

The bending has been done in a jig as shown in Fig. F. The material is bent in such a manner that the hardened area is placed in tension. It is realized that in these bend tests the shape of the fillet enters into the prob-

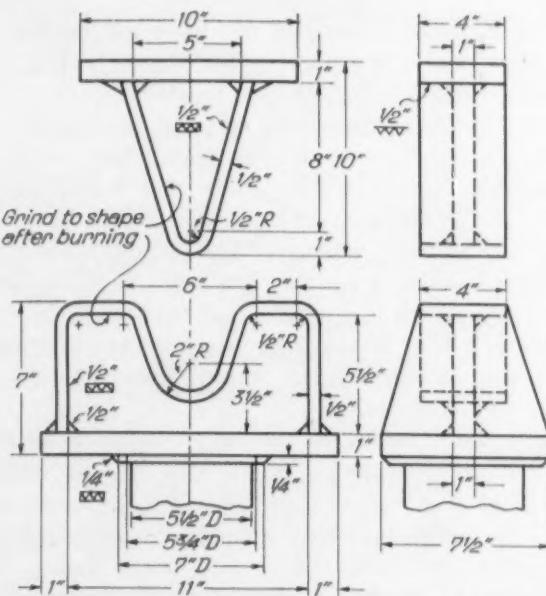


Fig. F—Showing Details of Fixture for Making Bend Tests.

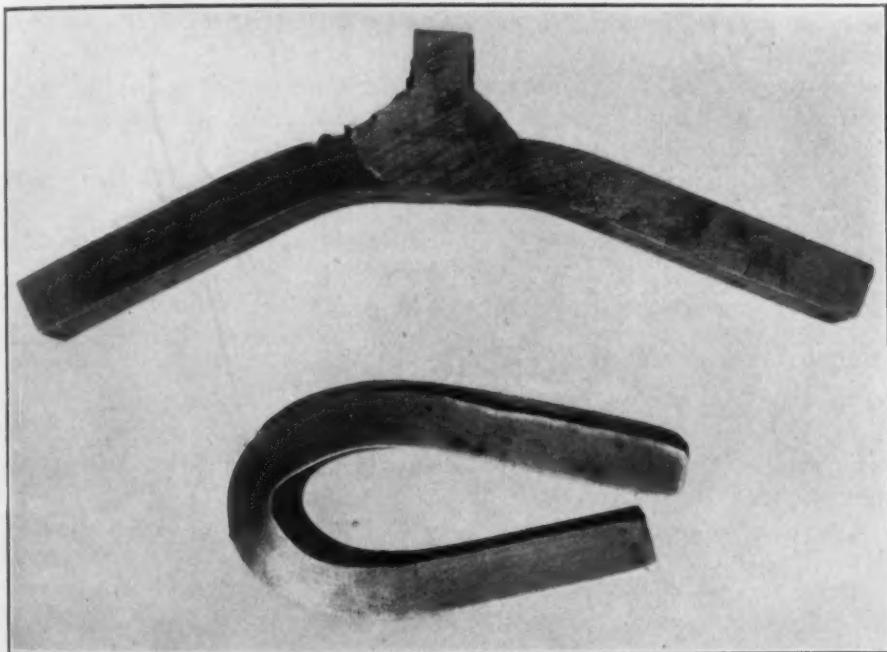


Fig. G—Photograph Showing the Effect of Welds in Bending of Specimens.

lem as well as a number of other variables, but if we do not use fillet welds we cannot get these failures.

A certain steel company sent in specimens which had been welded and had the welds machined off. It was contended that the bend test would be more

scientific and more accurate if we did not have the crudely shaped fillet on the specimen. The results are shown in Fig. G. The presence of the welds affects the bending greatly.

Some little time has been taken here to point out the use of this bend test in determining the satisfactoriness of a hardening base metal for welding because representations of the suitability of a base metal for welding are so often founded only on the results from butt welds. If a butt weld is made in a high tensile steel, and fracture occurs in base metal outside of the weld, the material is proclaimed satisfactory for welding. It is hoped that the fillet-welded specimens have shown that that is not necessarily true.

N. E. WOLDMAN:<sup>2</sup> Mr. Armstrong's paper on arc welding of high carbon and alloy steels is very interesting, but several statements are made which require further study and consideration.

Table III shows the effect of preheating on the Izod impact results of the alloy steel plate, and the statement is made that "at the welds impact values decreased as the preheating temperature increased." Again on page 581 the author states that "preheating not only affected the properties of the weld adversely but appeared to embrittle the steel in areas that were unaffected by the weld." These statements are contrary to what has been observed by others and to what is generally known in practice. The purpose of preheating is to decrease the rate of cooling of the weld and the affected zone so as to prevent or inhibit martensitic formation, thereby increasing the ductility and the impact value. The author shows by his illustrations that preheating to temperatures up to 1250 degrees Fahr. decreases the amount of martensitic formation and increases the amount of precipitated ferrite and pearlite in one form or another. And if he does obtain more pearlite and less martensite in the affected zone on preheating there is no reason why he should obtain lower impact values. Preheating at high temperatures below the critical should not embrittle the steel in areas that were unaffected by the weld. If a zone is unaffected by the weld it should also be unaffected by the preheat if the temperature of the preheat is kept below the tempering temperature.

The accompanying following curves for the physical properties of an oil-quenched and tempered S.A.E. 3335 steel show a marked increase in the Izod value as the steel is heated between 600 and 1200 degrees Fahr. This steel is very close to the composition of the plate used by the author in his experiments. Note that in this steel there is no temper brittleness at temperatures above 600 degrees Fahr.

A number of welding engineers have commercially adopted the scheme of preheating at various temperatures prior to welding to obtain higher impact values and also to decrease the tendency for cracks to develop in the affected areas. However, careful consideration must be given to those steels susceptible to temper brittleness.

The author further states that welding of high carbon and alloy steel (above 0.30 per cent carbon) is, at best, not satisfactory if the steel is to be used in structural members. This is true enough, but many machine parts and structural members of high carbon or alloy content can and have been satis-

<sup>2</sup>Metallurgist, Eclipse Aviation Corp., East Orange, N. J.

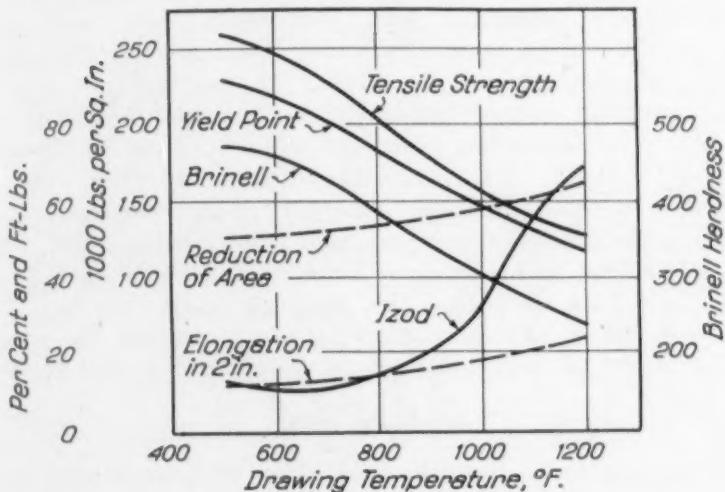


Fig. A—Physical Properties of an Oil-Quenched and Tempered S.A.E. 3335 Steel.

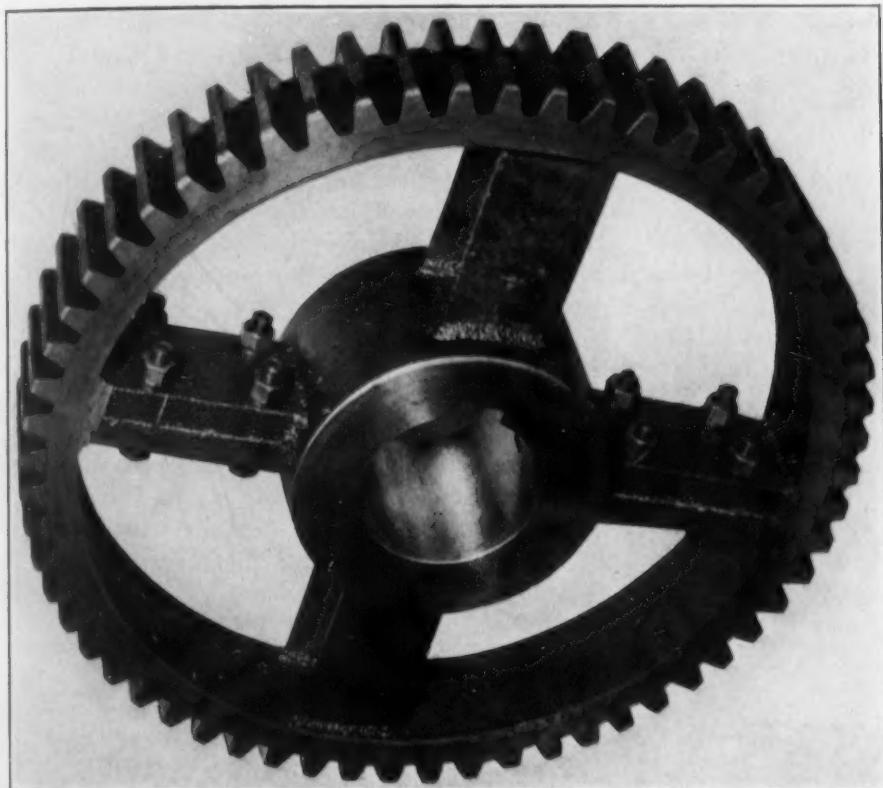


Fig. B—An All Welded Fabricated Gear of About Three Feet in Diameter.

factorily welded with proper welding technique. I wish to invite your attention to the accompanying illustration showing an all-welded fabricated gear

of about three feet in diameter. This is a split gear, having been made in two separate halves and bolted together as shown. The two half rims were forged and shaped from a 0.46 per cent carbon steel. The two half hubs were machined from a 0.33 per cent carbon steel casting. The arms were made from 0.12 per cent carbon steel hot-rolled plate. All arms were welded to the hub and to the rim as shown. No cracks developed during or after welding as the parts were preheated to 400 degrees Cent. (750 degrees Fahr.) prior to welding. After welding and assembly, the gear was finish machined and hobbed. It was then heat treated by quenching in brine solution and tempered to a hardness of 255 Brinell on the teeth. This gear was finally installed on an open-hearth steel charging machine driven by a 36 horsepower motor and functioned perfectly without failure in the welds or in areas adjacent to welds.

#### Author's Reply

Mr. McKinney, in his comment, stated that some electrodes such as the austenitic chromium-nickel steels are sometimes used successfully to prevent severe hardening under the weld as these electrodes require a much lower current density than mild steel to obtain satisfactory fusion and penetration. The author has tried this method and while the hardened zone may have been shallower there was still a definite martensitic area. The use of such electrode introduced an additional hazard. Quite often the deposit absorbs sufficient quantity of the base at the fusion zone to make this area martensitic also. It is obvious that any type of electrode that is used successfully will heat the base sufficiently to fuse the deposit. Unless the base is very small the mass of the base will hasten the cooling sufficiently to cause martensite. It is possible that the quantity of martensite formed can be controlled somewhat by welding technique and it is true that the atmospheric temperature is a factor, but the author doubts seriously if martensite can be eliminated entirely in steels of the composition used in this test unless the steel is preheated before arc welding.

Dr. Woldman states that decrease in Izod values in the base metal, due to preheating prior to welding is contrary to results observed by others. The author was skeptical himself until the tests were repeated and the same results obtained. Mr. McKinney apparently does not find these results surprising and he was correct in assuming the plate material was specially treated to resist high magnitude impact. In the paper it was stated that the reason for the Izod falling off was not determined and Mr. McKinney's explanation is the only one that can be offered at this time.

## THE INFLUENCE OF DEOXIDATION ON THE AGING OF MILD STEELS

BY B. N. DANILOFF, R. F. MEHL AND C. H. HERTY, JR.

### Abstract

*A series of steels, varying in carbon content between 0.02 and 0.25 per cent, and representing a wide variation in the degree of deoxidation, was tested for aging after quenching from subcritical temperatures and after cold working. According to the deoxidation treatment the steels were divided into four major classes: (1) rimmed steels, (2) semi-killed steels, (3) silicon-killed steels, and (4) aluminum-killed steels. It was found that deoxidation has a very pronounced effect on both types of aging. The tendency of steels to age was found to decrease with deoxidation in the order given above. Steels deoxidized with silico-manganese in the furnace and ferrosilicon and aluminum in the ladle were found to be practically non-aging. It is believed that deoxidation decreases the susceptibility of steels to aging directly through the decrease in dissolved oxygen content, and indirectly by virtue of its action in refining the grain-size of the steels.*

### INTRODUCTION

THE making of a heat of steel involves a number of complex physico-chemical processes both within and among the phases present in the furnace. Any variation in the interaction between the phases is necessarily reflected in the behavior of the finished heat of steel and in the quality of the finished solid ingot. One of the most important variables determining the quality of the finished steel is the method and degree of deoxidation of the steel, for this is known to exert a powerful influence on the response of the steel to

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This article is an abstract of a thesis submitted by B. N. Daniloff to the Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Science.

A paper presented before the Seventeenth Annual Convention of the Society held in Chicago, September 30 to October 4, 1935. Of the authors, B. N. Daniloff is Metallurgical Advisory Board Fellow and Graduate Student, Department of Metallurgical Engineering, Carnegie Institute of Technology, R. F. Mehl is Director, Metals Research Laboratory, and Professor of Metallurgy, Carnegie Institute of Technology, Pittsburgh, and C. H. Herty, Jr., is metallurgical engineer, Bethlehem Steel Co., Bethlehem, Pa. Manuscript received June 8, 1935.

a number of mechanical and thermal treatments, particularly its response to aging after cold working and to aging after quenching from subcritical temperatures. Inasmuch as aging may be regarded as either injurious or beneficial to steel, it is desirable to control the susceptibility of steel to aging and thus to enable the manufacturer deliberately to produce a steel that will or will not age to suit service requirements. Much is already known concerning the effect of deoxidation on aging, but in certain respects additional knowledge is needed. It is the purpose of the present paper to procure additional data on the aging behavior of steels deoxidized to different degrees.

The aging of steel after cold working has long been known,<sup>1,2</sup> though the mechanism has not been studied until recently and still presents several difficulties. In spite of the great amount of work done in the study of the constitution and heat treatment of steel, it was only recently that the phenomenon of the aging of steel after quenching from subcritical temperatures, similar to that of duralumin, was discovered. In 1927 Köster<sup>3</sup> and Masing and Koch<sup>4</sup> made the first careful investigation of this type of aging in steel. These workers have shown that the duralumin type of aging in steel is caused by the precipitation of carbides from ferrite, and that the phenomenon is entirely analogous to the aging of duralumin.

In 1923 Bean,<sup>5</sup> Sawyer,<sup>6</sup> and Fry<sup>7</sup> suggested the possibility of precipitation hardening in iron-nitrogen alloys, and Dean<sup>8</sup> in 1929 demonstrated age hardening of iron and steel caused by precipitation of nitrides.

Gumlich<sup>9</sup> as early as 1918 suggested that oxygen may be respon-

<sup>1</sup>C. E. Stromeyer, "The Aging of Mild Steel," *Journal, Iron and Steel Institute*, No. 1, 1907, p. 200-250.

<sup>2</sup>A. A. Stevenson, "Properties of Locomotive Tires Change with Age," *Metal Progress*, Vol. 20, 1931, p. 81-82.

<sup>3</sup>W. Köster, "Stahl und Eisen als Werkstoff," *Vorträge Werkstofftagung*, 1927, Vol. 3, p. 16, also *Archiv. für das Eisenhüttenwesen*, Vol. 2, 1928-29, p. 194-5.

<sup>4</sup>G. Masing and L. Koch, "Duraluminartige Vergütung bei Eisen-Kohlenstofflegierungen," *Wiss. Veröff. a. d. Siemens Konsern*, Vol. 6, 1927, p. 202-210.

<sup>5</sup>W. R. Bean, "Deterioration of Malleable in Hot-Dip Galvanizing Process," *Transactions, American Institute of Mining and Metallurgical Engineers*, Vol. 69, 1923, p. 895.

<sup>6</sup>C. B. Sawyer, "Early Work on Iron-Nitrogen Equilibrium," *Metal Progress*, Vol. 19, 1931, p. 89-90. Also, "Nitrogen in Steel," *Transactions, American Institute of Mining and Metallurgical Engineers*, Vol. 49, 1923, p. 799.

<sup>7</sup>A. Fry, "Stickstoff in Eisen, Stahl und Sonderstahl," *Kruppsche Monatshefte*, Vol. 4, 1923, p. 137-151.

<sup>8</sup>R. S. Dean, R. O. Day and J. L. Gregg, "Relation of Nitrogen to Blue-Heat Phenomena and Dispersion Hardening in the System Fe-N," *American Institute of Mining and Metallurgical Engineers, Tech. Pub. No. 193*, 1929.

<sup>9</sup>E. Gumlich, "Ueber die Abhängigkeit der Magnetischen Eigenschaften des Spezifischen Widerstandes unter der Dichte der Eisenlegierungen von der Chemischen Zusammensetzung und der thermischen Behandlung," *Wiss. Abhandl. Phys. Techn. Reichsanst.*, Vol. 4, 1918, p. 267-420.

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sible for magnetic aging of iron. The study of over-strain aging of steel by Pfeil<sup>10</sup> in 1928 suggested that the precipitation of oxides may be responsible for aging after cold working. Later investigators have suggested that precipitation of oxides has an effect on both over-strain and quench aging in many respects similar to that of carbon. At the present it seems possible that the elements carbon, nitrogen, and oxygen may act as hardening elements in both types of aging in steel.

The data available on the solubility of oxygen in solid iron are somewhat scarce and lacking in agreement.<sup>11, 12, 13, 14, 15, 16, 17, 18</sup> The iron-oxygen diagram has been worked out by Tritton and Hanson<sup>19</sup> and several of its modifications have been published.<sup>20, 21, 22, 23, 24</sup> Despite the disagreement in the results on the exact values of the solubility of oxygen in alpha iron, it seems likely that this solubility decreases with decreasing temperature, thus satisfying the principal requirement for precipitation hardening.

Eilender and Wasmuht<sup>25</sup> studied the quench aging of alloys

<sup>10</sup>L. B. Pfeil, "The Change in Tensile Strength Due to Aging of Cold-Drawn Iron and Steel," *Journal*, Iron and Steel Institute, Vol. 118, No. 2, 1928, p. 167-181; disc. *ibid.* p. 182-194.

<sup>11</sup>F. Tritton and D. Hanson, "Iron and Oxygen," *Journal*, Iron and Steel Institute, Vol. 110, No. 2, 1924, p. 99-121.

<sup>12</sup>W. Krings and J. Kempkens, "Ueber die Löslichkeit der Sauerstoffs in festen Eisen," *Zeit. anorg. Chemie.*, Vol. 183, 1929, p. 225-250.

<sup>13</sup>W. Eilender and R. Wasmuht, "Ein Beitrag zur frage der Ausscheidungshärtung des Eisens," *Archiv f. d. Eisenhüttenwesen*, Vol. 3, 1930, p. 659-664.

<sup>14</sup>L. Jordan and J. R. Eckman, "Gases in Metals, II. The Determination of Oxygen and Hydrogen in Metals by Fusion in Vacuum," U. S. Bureau of Standards, Scientific Paper No. 314, 1925.

<sup>15</sup>A. Wimmer, "Ueber den Einfluss des Sauerstoffs auf die physikalischen und Technischen Eigenschaften des Flusseisens," *Stahl und Eisen*, Vol. 45, 1925, p. 73-79.

<sup>16</sup>J. Reschka, "Beitrag zur Frage des Sauerstoffs im Eisen," *Mitt. a. d. Forschungsinstitut der Vereinigte Stahlwerke A. G.*, Vol. 3, 1932, p. 1-18.

<sup>17</sup>H. Schenck and E. Hengler, "Untersuchungen über das System Eisen-Sauerstoff," *Archiv f. d. Eisenhüttenwesen*, Vol. 5, 1931, p. 209-214.

<sup>18</sup>N. A. Ziegler, "Solubility of Oxygen in Solid Iron," *TRANSACTIONS, American Society for Steel Treating*, Vol. 20, 1932, p. 73-82.

<sup>19</sup>Ref. 11.

<sup>20</sup>K. Schönert, "Beitrag zur System: Eisen-Sauerstoff," *Zeit. für anorg. und allgem. Chemie*, Vol. 154, 1926, p. 220-225.

<sup>21</sup>H. Schenck, "Physikalische Chemie der Eisenhüttenprozesse," Julius Springer, Berlin, 1932, Vol. 1, p. 131.

<sup>22</sup>H. Esser and H. Cornelius, "Gefügeuntersuchung bei Temperaturen bis Temperaturen bis 1100°," *Stahl und Eisen*, Vol. 53, 1933, p. 532-535. Also *Metals and Alloys*, Vol. 4, 1933, p. 119-122.

<sup>23</sup>C. Benedicks and H. Löfquist, "Non-metallic Inclusions in Iron and Steel," Stockholm, 1930, p. 56.

<sup>24</sup>E. R. Jette and F. Foote, "An X-ray Study of the Wüstite (FeO) Solid Solutions," *Journal of Chemistry and Physics*, Vol. 1, 1933, p. 29-36. "A Study of Homogeneity Limits of Wüstite (FeO) by X-ray Methods," *Transactions, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division*, Vol. 105, 1933, p. 276-289.

<sup>25</sup>Ref. 13.

prepared by melting iron in a hydrogen atmosphere and introducing the desired amounts of oxygen by remelting in air. They found no appreciable hardening in specimens with the oxygen content below 0.035 per cent upon quenching from 680 degrees Cent. (1255 degrees Fahr.) followed by aging at room temperature. With rising oxygen content the hardening increased to a maximum (56.5 per cent) in specimens with 0.06 per cent oxygen. With further increase in the oxygen content the hardening decreased, but was still greater than that of the low oxygen alloys. These workers also found that the maximum hardness is obtained on room temperature aging; at higher temperatures the maximum hardening is less, but is reached more rapidly as the temperature increases. This behavior is very similar to that of pure iron-carbon and iron-nitrogen alloys, and this was interpreted as indicating that the aging of iron-oxygen alloys is due to the same process, namely, the precipitation of oxides from solid solution.

According to data published by Pickard<sup>26</sup> the average oxygen content of some commercial irons and steels as determined by the hydrogen reduction method is as follows:

Acid open-hearth .....	0.010 per cent O <sub>2</sub>
Basic open-hearth .....	0.019 per cent O <sub>2</sub>
Ingot iron (American) .....	0.092 per cent O <sub>2</sub>
Ingot iron (English) before deoxidation	0.092 per cent O <sub>2</sub>

Grossmann<sup>27</sup> gave the following values of oxygen content, determined by vacuum fusion, of a few commercial irons and steels:

	Composition, Per Cent			
	Carbon	Manganese	Silicon	Oxygen
Carbon steel .....	0.19	0.37	0.11	0.008
Soft steel .....	0.03	0.18	0.01	{ Rim 0.019 Core 0.068
Open-hearth iron..	0.02	0.03	0.005	{ Rim 0.047 Core 0.103

These figures refer to commercial steels cast into ingots weighing from 1½ to 5 tons.

The oxygen content of some of the materials quoted is sufficiently high to form supersaturated solid solution of oxygen in

<sup>26</sup>J. A. Pickard, "The Oxygen Content of Iron and Steel and Its Effect on Their Properties," British Iron and Steel Institute, Carnegie Scholarship Memoirs, Vol. 7, 1916, p. 68-82.

<sup>27</sup>M. A. Grossmann, "Oxygen in Steel" (Fifth Campbell Memorial Lecture), American Society for Steel Treating, 1930.

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alpha iron. Even in those steels in which the oxygen appears to be below the solubility limit generally accepted, it may be at least partly responsible for aging in the presence of carbon and nitrogen, or after cold working.

Although the effect of oxygen on the aging of iron and steel has been noted long ago<sup>28</sup> and many references thereon are found in the literature, the role of oxygen does not appear to be perfectly understood, and still is a subject of much controversy. Pfeil,<sup>29</sup> Oberhoffer,<sup>30</sup> and von Koeckritz<sup>31</sup> suggested that oxygen in commercial steels might be a factor contributing to aging. On the other hand Eilender and Wasmuht,<sup>32</sup> Eilender, Fry, and Gottwald,<sup>33</sup> and Esser and Cornelius<sup>34</sup> believe that oxygen in commercial steels bears little or no relation to the aging. Sauveur<sup>35</sup> has stated that the part played by oxygen in commercial steels is still in doubt.

The work of Köster<sup>36</sup> has shown that although carbon and nitrogen precipitate independently, the carbon in solution delays the precipitation of nitrogen, and that if carbon in solution exceeds a certain amount the precipitation of nitrogen can be completely suppressed. On the other hand, oxygen has been reported to have the opposite effect, namely, to promote the precipitation of nitrogen.<sup>37</sup> Oxygen apparently influences the precipitation of both carbon and nitrogen.<sup>38</sup> The solubility of carbon in alpha iron is probably decreased by oxygen,<sup>39</sup> and conversely, carbon reduces the solubility of oxygen in alpha iron.

It has been stated by several investigators that melting has a

<sup>28</sup>Ref. 9.

<sup>29</sup>Ref. 10.

<sup>30</sup>P. Oberhoffer, H. J. Schiffler and W. Hessenbruch, "Sauerstoff in Eisen und Stahl," *Stahl und Eisen*, Vol. 47, 1927, p. 1540-1543.

<sup>31</sup>H. von Koeckritz, "Ueber Zeitlichen Verlauf der Alterung weichen Stahls und über die Alterung von Stählen Verschiedener Herkunft," *Mitl. aus der Forschungsinstitut der Vereinigte Stahlwerke*, A. G., Vol. 2, No. 2, 1932, p. 193-222.

<sup>32</sup>Ref. 13.

<sup>33</sup>W. Eilender, A. Fry and A. Gottwald, "Einfluss verschiedener Elemente auf die Ausscheidungsvorgänge im Stahl beim Anlassen," *Stahl und Eisen*, Vol. 54, 1934, p. 554-564.

<sup>34</sup>Ref. 22.

<sup>35</sup>A. Sauveur, "Notes on the Aging of Metals and Alloys," *TRANSACTIONS, American Society for Metals*, Vol. 22, 1934, p. 97-119.

<sup>36</sup>W. Köster, "Zur Frage des Stickstoffs im Technischen Eisen," *Archiv f. d. Eisenhüttenwesen*, Vol. 3, 1930, p. 637-655. Discussion p. 655-658.

<sup>37</sup>Ref. 30.

<sup>38</sup>Ref. 33.

<sup>39</sup>L. R. Van Wert, "Some Notes on Blue Brittleness," *Transactions, American Institute of Mining and Metallurgical Engineers*, Iron and Steel Division, 1931, p. 230-246.

considerable influence on the tendency of steel for aging.<sup>40, 41</sup> Wilhelm and Jahn<sup>42</sup> from the results of many tests concluded that steels made from scrap possess the same aging tendency as steels made from other materials, i.e., the high scrap content does not increase the aging ability of the steel. Walzel<sup>43, 44</sup> however, has claimed that pig iron in the furnace charge decreases the susceptibility of steel to aging.

Gumlich<sup>45</sup> pointed out in 1918 that additions of aluminum and silicon suppress the tendency of steel to age magnetically. Fry<sup>46</sup> reported that MnO has a great effect on the sensitivity of steel to aging. According to Fry, MnO is soluble to a considerable extent in iron at about 700 degrees Cent. (1290 degrees Fahr.) and on slow cooling is precipitated in a fine state of dispersion. On the other hand, if oxygen is present in the form of iron silicate or silica, which are less soluble in iron than MnO, its effect on aging is considerably smaller. The effect of oxygen is indeed small when it is present as  $Al_2O_3$  because alumina is practically insoluble in iron. Fry stated that soft steel deoxidized with aluminum and containing 0.05 per cent excess aluminum is non-aging.

Experiments reported by Diergarten<sup>47</sup> show that steels deoxidized with manganese and silicon are very susceptible to aging. Steels deoxidized with aluminum were found to age very little at 300 degrees Cent. (570 degrees Fahr.), though the total oxygen content was the same in both steels. It was concluded that deoxidation with aluminum is essential for the production of a non-aging steel.

Oertel and Schepers<sup>48</sup> studied two low carbon steels (0.07 and

<sup>40</sup>Ref. 31.

<sup>41</sup>F. Roetscher and M. Fink, "Beitrag zur Kerbzähigkeit hochwertiger Baustähle," *Zeit des Vereins deutscher Ing.*, Vol. 76, 1932, p. 173-177.

<sup>42</sup>H. Wilhelm and L. Jahn, "Alterungskerbzähigkeit des aus Schrott erschmolzenen Siemens-Martin Stahls," *Archiv f. d. Eisenhüttenwesen*, Vol. 7, 1933, p. 201-203.

<sup>43</sup>R. Walzel, "Eine besondere Ausführungsform des Kerbschlagversuches angewendet für den Vergleich der Alterungsempfindlichkeit von Stählen," International Association for Testing Materials, Zurich Meeting, 1931, Vol. 1, 1932, p. 405-408.

<sup>44</sup>R. Walzel, "Beitrag zur Kenntnis der Mechanischen Alterung weichen Flusstahls," *Archiv f. d. Eisenhüttenwesen*, Vol. 6, 1932, p. 257-262.

<sup>45</sup>Ref. 9.

<sup>46</sup>See disc. on p. 735 of paper by P. Oberhoffer, H. Hochstein and W. Hessenbruch, "Sauerstoff in Eisen und Stahl. II. Der Einfluss des Sauerstoffs auf das Gefüge und einige Eigenschaften verschiedener Baustähle," *Archiv f. d. Eisenhüttenwesen*, Vol. 2, 1929, p. 725-738.

<sup>47</sup>Ref. 46.

<sup>48</sup>W. Oertel and A. Schepers, "Eigenschaften beruhigt und unberuhigt vergossenen Stahles," *Stahl und Eisen*, Vol. 51, 1931, p. 710-715.

0.08 per cent carbon), one of which had been deoxidized with 0.10 per cent silicon. Impact tests made on specimens cold-worked 15 per cent by tension and heated at various temperatures showed that the steel deoxidized with silicon aged less than the rimmed steel. Magnetic tests on the same steels after quenching from 600 degrees Cent. (1110 degrees Fahr.) and aging at various temperatures showed no appreciable difference in the changes in coercive force and residual magnetization; likewise, no difference was observed in the deep drawing properties of the two steels. Pomp and Klein<sup>49</sup> also noted that deoxidized basic Bessemer (Thomas) steel ages less than similar steel which has not been deoxidized. Köster<sup>50</sup> reported that Thomas and electric steels age more than Siemens-Martin steels because they absorb more nitrogen during the manufacture. This worker also believed that silicon- and aluminum-killed steels retained more nitrogen in solution and consequently age less than unkilled steels. Hayes<sup>51, 52</sup> reported the development of a non-aging steel deoxidized with aluminum and titanium. This steel after proper heat treatment is free from aging, blue brittleness, and (after proper pre-straining) stretcher-straining.

In spite of the contradictions regarding the effect of oxygen on aging, the published statements on the efficacy of deoxidation are in agreement, all indicating that deoxidation decreases the susceptibility of steel to aging. Since deoxidation has certain secondary effects on the steel, other possible phenomena connected with deoxidation should not be disregarded in this connection.

One of these secondary effects is the diminution of grain-size of steels, particularly in those deoxidized with aluminum. Certain investigators have stated that oxygen in steel tends to increase the grain-size;<sup>53, 54, 55</sup> deoxidation, on the other hand, decreases the grain-size and inhibits or in some cases entirely prevents grain growth.<sup>56, 57</sup>

<sup>49</sup>A. Pomp and O. Klein, "Ueber die Alterung von Feinblechen aus Flüssstahl," *Mitt. a. d. Kaiser Wilhelm Inst.*, Vol. 15, 1933, p. 205-245.

<sup>50</sup>Ref. 36.

<sup>51</sup>A. Hayes and R. O. Griffis, "Non-Aging Iron and Steel for Deep Drawing," *Metals and Alloys*, Vol. 5, 1934, p. 110-112.

<sup>52</sup>Anon. Announces a New Deep Drawing Steel, *Iron Age*, Vol. 132, 1933, p. 27-28.

<sup>53</sup>Ref. 11.

<sup>54</sup>Ref. 15.

<sup>55</sup>Ref. 30.

<sup>56</sup>Ref. 48.

<sup>57</sup>C. H. Herty, Jr., D. L. McBride and S. Hough, "Effect of Deoxidation on Grain Growth in Plain Carbon Steel," *Cooperative Bulletin 65*, Carnegie Institute of Technology, 1934.

There is little information in the literature regarding the effect of grain-size on the aging. Köster<sup>58</sup> reported that the aging capacity is independent of the grain-size, though the yield point elongation increases as the grain-size decreases. Walzel<sup>59</sup> found that grain-size differences produced by heat treatment have an appreciable effect, the aging tendency decreasing with decreasing grain-size. On the other hand, it has been reported that the decrease in grain-size results in an increase in the amount and rate of precipitation hardening.<sup>60</sup> It is apparent that the evidence is far from being conclusive, and the question of the effect of grain-size needs further study.

Another secondary effect of deoxidation has been considered in the literature, namely, the "deactivation" of nitrides. Tschischevsky<sup>61</sup> in 1915 found that aluminum when added to molten steel combines with nitrogen to form a stable nitride of aluminum. Recently Eilender, Fry and Gottwald<sup>62</sup> in a very complete paper found that aluminum, titanium, zirconium, and vanadium suppress the ability of steels to quench-age as soon as their concentration is sufficient to react with all of the nitrogen to form their nitrides. It was also found that zirconium, titanium, and vanadium will "deactivate" the carbon.

It appears, therefore, that the function of deoxidation, with respect to aging, is not only to remove the oxygen but also to furnish elements which will combine with the nitrogen and the carbon in the steel.

Only the three common deoxidizers, manganese, silicon, and aluminum, were used in the preparation of the steels used in this work, and consequently the discussion of deoxidation may be limited to these three deoxidizers.

It is known from the work of Herty<sup>63</sup> and of Chipman<sup>64</sup> that the relative deoxidizing powers of aluminum, silicon, and manganese are in the order stated. Very small amounts of residual aluminum are

<sup>58</sup>W. Köster, "Der Einfluss einer Wärmebehandlung unterhalb A<sub>1</sub> auf die Eigenschaften des Technischen Eisens," *Archiv f. d. Eisenhüttenwesen*, Vol. 2, 1929, p. 503-522.

<sup>59</sup>Ref. 44.

<sup>60</sup>V. N. Krivobok, Reference to work of Söhnchen cited by Dr. Krivobok in his discussion of Cooperative Bulletin 66, Feb., 1934.

<sup>61</sup>N. Tschischevsky, "The Occurrence and Influence of Nitrogen on Iron and Steel," *Journal*, Iron and Steel Institute, Vol. 92, No. 2, 1915, p. 47-49; disc. p. 98-105.

<sup>62</sup>Ref. 33.

<sup>63</sup>C. H. Herty, Jr., "The Deoxidation of Steel," Cooperative Bulletin 69, Carnegie Institute of Technology, 1934.

<sup>64</sup>John Chipman, "Application of Thermodynamics to the Deoxidation of Liquid Steels," *TRANSACTIONS, American Society for Metals*, Vol. 22, 1934, p. 385-446.

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required to reduce the residual iron oxide to extremely low concentrations. Manganese is the weakest of the three deoxidizers, and will leave relative high amounts of oxygen in the steel, whereas silicon will leave an intermediate amount. The exact relationships between residual oxygen and residual alloyed deoxidizers may be found in the papers by Herty and by Chipman cited above.

When more than one of these are used, the deoxidation reactions are complicated by the presence of several oxides. The purpose of using combinations of various deoxidizers is to obtain deoxidation products which will coagulate into larger particles, and thus tend to be removed by levitation. In the aluminum-killed steels a very fine suspension of alumina particles is formed, even in the presence of other residual materials produced by the use of manganese and silicon as deoxidizers, owing to the low fluxing power of alumina. These particles do not grow or coalesce owing to their refractory nature, and therefore remain suspended in the metal, persisting through all the subsequent processing of the steel, and thus appearing in the final steel.

#### SCOPE OF INVESTIGATION

The primary purpose of this investigation is to make a comprehensive study of the influence of variations in the deoxidation practice on both the quench and the overstrain aging of commercial mild steels. Furthermore, because deoxidation exerts secondary effects on steel, other factors, such as grain-size, "deactivation" of nitrides and carbides, and the role of finely dispersed particles of deoxidation products, are considered.

Strain and quench aging tests were performed on 34 steels of various degrees of deoxidation and of varying carbon content. Quench hardness tests were made with the purpose of ascertaining whether the increased hardness upon quenching from increasing subcritical temperatures, presumably indicating an increasing concentration of solid solution, is accompanied by increased tendency of steels to age, and thus to obtain some insight into the mechanism of aging.

Additional tests were made on the influence of grain-size on aging in order to determine what effect the grain-size has on the quench and overstrain aging and also to ascertain the degree to which the finer grain-size of aluminum-killed steels may be responsible for their greater immunity to aging.

Tests were also made to ascertain whether a treatment at sub-critical temperatures might not alter the response of these steels to an over-strain aging treatment (inasmuch as this effect has been suggested).

Aging tests at elevated temperatures were made on a few selected steels in order to obtain an idea of the influence of time and temperature on the aging of steels representing extremes in the degree of deoxidation, and, incidentally, to attempt to differentiate between the age-hardening due to the precipitation of carbon and that due to the precipitation of oxygen.

### MATERIALS

For the determination of the effect of deoxidation on aging a set of steels was selected representing a wide variation in the degree and methods of deoxidation. Four classes of materials were selected as follows: (1) rimmed steels, (2) semi-killed steels, (3) silicon-killed steels, and (4) aluminum-killed steels. The carbon varied from 0.02 to 0.25 per cent, though unfortunately, it was impossible to obtain a complete range of carbon in each of the four types represented. The steels were commercial open-hearth steels, most of the heats having been made under the supervision of C. H. Herty, Jr. The electric furnace steels were experimental, and also made under the supervision of C. H. Herty, Jr. The analyses of the steels are given in Table I.

The method of deoxidation was chosen as the main variable determining the aging characteristics, and accordingly the steels were classified into the four groups indicated above. No attempt was made to classify the steels according to the oxygen content. Although the analyses given in Table I discriminate the four groups according to the oxygen content, they are not sufficiently reliable to justify arranging the steels according to the oxygen content within each group. The table shows that the oxygen content of the rimmed steels is considerably higher than that of the killed steels, and that the "SMA" steels, deoxidized with silico-manganese and aluminum, contain a negligible amount of oxygen, practically all of which is probably present in the form of  $Al_2O_3$ ; the amount of dissolved oxygen, if any, is very probably too low to be precipitated by any aging treatment.

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Table I  
Analysis of Steels Used

Sample No.	C	Mn	F	S	Per Cent Si	Al	N <sub>2</sub>	FeO†	O <sub>2</sub> ‡
<i>Rimmed Steels</i>									
2	0.044	0.33	0.009	0.025	0.004	.....	0.004	0.034	.....
13	0.044	0.35	0.013	0.035	0.007	.....	0.004	.....	.....
14	0.020	0.10	0.008	0.043	0.004	0.007	0.007	0.024	.....
16	0.148	0.53	.....	0.037	0.007	.....	0.005	0.046	.....
17	0.056	0.40	0.016	.....	.....	0.007	.....	0.046	.....
18	0.046	0.29	0.012	.....	.....	0.007	.....	.....	.....
19	0.110	0.44	0.009	.....	.....	.....	.....	0.037	.....
20	0.140	0.51	0.021	.....	.....	.....	.....	0.027	.....
<i>Semi-Killed Steels</i>									
4	0.192	0.77	0.020	0.045	0.013	0.009	0.008	.....	.....
6	0.260	0.63	0.018	0.035	0.017	0.012	0.004	.....	.....
7	0.094	0.35	0.012	0.038	0.007	.....	0.004	0.018	.....
8	0.150	0.42	0.027	0.045	0.002	0.014	0.005	.....	.....
K-7	0.154	0.56	0.240	0.040	0.074	0.010	.....	0.021	.....
<i>Silicon-Killed Steels</i>									
12	0.223	0.55	0.030	0.038	0.150	None	0.007	.....	.....
AX	0.310	0.43	0.016	0.043	0.111	.....	.....	0.020	.....
<i>Aluminum-Killed Steels</i>									
5	0.194	0.46	0.010	0.028	0.079	0.025	0.005	.....	.....
9	0.133	0.40	0.010	0.027	0.042	0.027	0.009	.....	.....
11	0.247	0.58	0.012	0.029	0.124	0.047	0.007	0.015	.....
Izett	0.141	0.44	.....	.....	0.067	0.038	.....	.....	.....
K-3*	0.097	0.50	0.015	0.034	0.031	0.038	.....	.....	.....
K-10*	0.138	0.49	0.023	0.022	0.066	0.039	.....	.....	.....
SMA-17	0.167	0.56	0.026	0.028	0.150	0.038	(Ni-0.26)	0.021	0.0023
SMA-22	0.214	0.58	0.020	0.043	0.088	0.033	.....	0.018	0.0015
SMA-15	0.150	0.71	0.011	0.029	0.074	0.025	.....	0.015	0.0013
K-13	0.240	0.43	0.009	0.023	0.015	0.018	.....	0.016	.....
K-14	0.190	0.46	0.006	0.034	0.005	0.030	.....	0.012	.....
AB	0.210	0.44	0.006	0.020	0.089	0.018	.....	.....	.....
AC	0.210	0.45	0.011	0.023	0.108	0.027	.....	.....	.....
<i>Electric Furnace Steels</i>									
Sample No.	C	Mn	P	S	Si	Al	Deoxidized With		
1-39	0.019	0.03	0.006	0.032	0.001	0.016	Al		
41	0.042	0.04	0.005	0.037	0.014	0.056	Al		
42	0.042	0.07	0.006	0.043	0.004	0.069	Al		
44	0.042	0.05	0.007	0.043	0.067	.....	Si		
46	0.040	0.06	0.006	0.036	0.163	.....	Si		
48	0.036	0.05	0.013	0.037	0.064	0.022	Si-Al		
52	0.167	0.15	0.026	0.037	0.001	0.140	Al		
56	0.170	0.60	0.028	0.037	0.178	.....	Mn-Si		

\*Normalized Izett steel plates.

†Determined by electrolytic-iodine method.

‡Determined by vacuum fusion method.

The rimmed steels were deoxidized with manganese in the furnace, and small amounts of ferromanganese were added in the ladle if reoxidation of the metal in the furnace had taken place after deoxidation. Small amounts of aluminum were added to molds, not exceeding  $\frac{1}{2}$  pound per ton. This amount is not sufficient to cause a pronounced change in the FeO content of the metal; it was added

merely to regulate the rate of gas evolution during freezing.<sup>65, 66</sup> To some of the rimmed steels (steels 2 and 17) small amounts of titanium (about 0.01 per cent of the charge weight) were added. As titanium is a much weaker deoxidizer<sup>67</sup> than aluminum, these additions should not result in any great variations in the degree of deoxidation. The semi-killed steels were deoxidized with manganese and silicon in the ladle, and some aluminum was added in the molds. The silicon-killed steels were deoxidized with manganese and silicon in the ladle. The aluminum-killed steels were deoxidized with silicon and manganese in the furnace and aluminum in the ladle. Steel K-13 was deoxidized with manganese and aluminum in the ladle with no previous furnace deoxidation. Steel K-14 was deoxidized with manganese in the furnace and aluminum in the ladle. No silicon was used in these steels in conjunction with aluminum.

The SMA steels were made to contain the minimum possible amount of dissolved iron oxide. The heats were killed in the furnace with silicomanganese (manganese 67 to 69 per cent, silicon 13 to 15 per cent). The silicon addition as silicomanganese amounted to 0.10 to 0.11 per cent of the weight of the metal and the manganese to about 0.48 per cent. Any additional manganese necessary to meet specifications was added as ferromanganese about 5 minutes after the silicomanganese addition. The heats were tapped from 10 to 15 minutes after the silicomanganese addition, and 0.05 and 0.10 per cent of silicon as ferrosilicon and 2 pounds of aluminum per ton were added in the ladle. The types and amounts of deoxidizers used are given in Table II, and the analyses of deoxidizers in Table III. The slag analyses of some of the steels before deoxidation are given in Table IV.

The grain-size of a few steels, representative of the four classes, is shown in Fig. 1. The photomicrographs were taken at 100 diameters on normalized steels.

#### METHODS

For the quench-aging tests small plates,  $\frac{1}{2}$  inch thick, were normalized, and about  $\frac{1}{8}$  inch was ground off the original surface. These specimens were then heated at 700 degrees Cent. (1290 degrees

<sup>65</sup>Ref. 63.

<sup>66</sup>C. F. Christopher, H. Freeman and C. H. Herty, Jr., "The Control of Iron Oxide in the Basic Open-hearth Process," Cooperative Bulletin 68, Carnegie Institute of Technology, 1934.

<sup>67</sup>Ref. 64.

Table II  
Deoxidizers Added to Furnace, Ladle and Mold

Steel	Mn (as Mn-Si Alloy)	Furnace		Ladle Per Cent			Mold	
		Si	Al	Mn (as Fe Mn)	Si	Al	Mn	Coal
<i>Rimmed Steels</i>								
2	0.170	0.037	.....	.....	.....	0.0060	0.270	.....
17	0.096	0.060	.....	.....	.....	0.0047	0.185	.....
20	.....	.....	.....	0.18	.....	.....	0.500	0.03
<i>Semi-Killed Steels</i>								
7	0.45	0.10	.....	0.06	.....	.....	.....	.....
8	0.45	0.10	.....	0.18	.....	.....	.....	.....
K-7	None	None	.....	None	0.12	None	0.50	0.03
4	0.40†	.....	.....	0.60	.....	.....	0.05	0.005
6	0.45	0.10	.....	0.18	.....	.....	.....	.....
<i>Silicon-Killed Steels</i>								
I-46	.....	.....	.....	.....	0.018	.....	.....	.....
I-44	.....	.....	None	.....	0.009	.....	.....	.....
AX	None	None	None	None	0.220	None	0.40	None
12	0.07	0.25†	.....	0.11	0.120	.....	0.04	.....
<i>Aluminum-Killed Steels</i>								
I-39	.....	.....	.....	.....	.....	0.004	.....	.....
I-48	.....	.....	.....	.....	0.006	0.003	.....	.....
I-41	.....	.....	.....	.....	.....	0.013	.....	.....
I-42	.....	.....	.....	.....	.....	0.011	.....	.....
SMA-15	0.46	0.103*	None	0.160	0.05	0.086	0.130	None
SMA-17	0.45	0.100*	None	0.150	0.10	0.092	None	0.05
5	0.52	0.118*	.....	0.064	0.10	0.090	0.056	0.17
SMA-22	0.45	0.100*	None	0.090	0.05	0.092	0.030	0.03
11(G)	0.40	0.078*	None	0.060	0.09	0.080	None	None

\*As Silico-Manganese.

†As Spiegeleisen.

Fahr.) for 1 hour, and quenched in oil. For quenching temperatures below 700 degrees Cent. (1290 degrees Fahr.) the samples were left at temperatures for longer time. The surfaces were immediately reground and Rockwell "B" hardness readings were taken immediately and after various periods of aging at room temperature.

The strain aging was studied by means of both hardness and impact (Izod and Charpy, V-notch) tests. The method employed by Bauer<sup>68</sup> was used, in which the impact test pieces were machined to predetermined oversize dimensions and compressed by means of a tool-steel die in order to obtain various degrees of reduction in thickness. Two sets of tests were run: in the first set the specimens were compressed 15 per cent and aged at 450 degrees Cent. (840 degrees Fahr.) in a lead bath; in the second set the specimens were compressed 2 per cent and aged at 100 degrees Cent. for various lengths

<sup>68</sup>O. Bauer, "Gering alterungsempfindliche Stähle," *Zeit. Bayerischen Revisionsverein*, Vol. 32, 1928, p. 23.

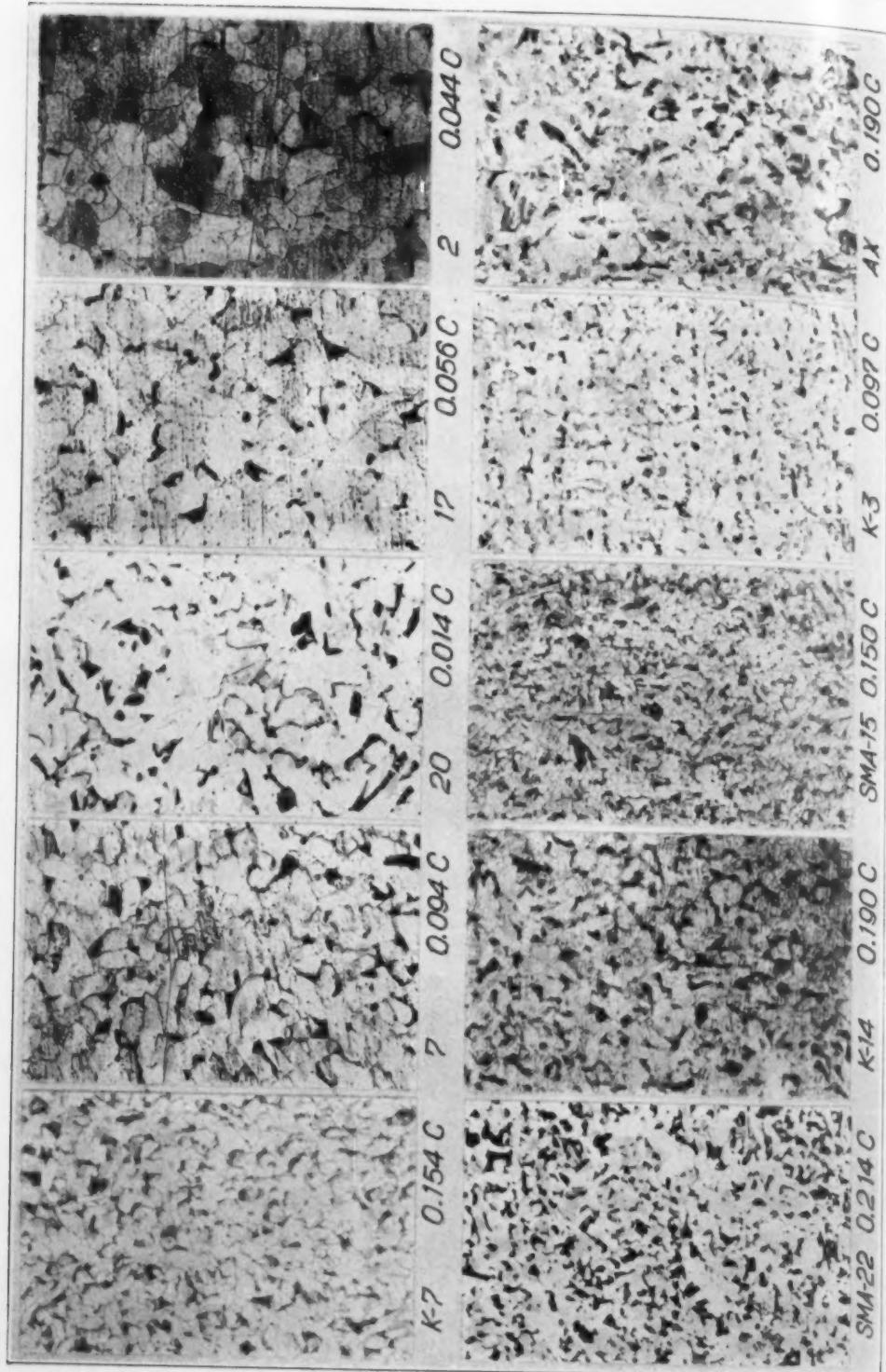


Fig. 1—Microstructure of Normalized Steels.  $\times 100$ . K-7, 7—Semi-killed; 2, 17, 20—Rimmed; AX—Rimmed; SMA-15, K-14, SMA-22—Aluminum-killed.

Table III  
Analyses of Deoxidizers Used

	Mn	Si	Al	Per Cent
Common Spiegel	20.0	1.5	...	4.00
High Silicon Spiegel	21.0	4.0	...	4.25
Silico-Manganese	69.0	15.5	...	2.50
Ferromanganese	80.0	0.6	...	6.50
Ferrosilicon	...	50.0	...	...
Alsifer	...	40.0	20.0	...
Aluminum	...	...	98.0	...

of time. On the latter set Rockwell hardness tests were also made directly on the compressed portions of the impact specimens prior to breaking the specimens in the impact machine.

### RESULTS AND DISCUSSION

The results of the tests on quench aging are given in Figs. 2 to 6 and Table V. The steels are divided into rimmed, semi-killed, silicon-killed, and aluminum-killed, each group arranged in the order of increasing carbon content.

#### Quench Aging

(a) *Rimmed Steels.* In Fig. 2 all the steels in this group showed a great susceptibility to quench aging. The maximum hardening was obtained in the steels containing 0.04 to 0.05 per cent carbon. As may be seen from Table V the rimmed steels of lower carbon content (steels 13, 2, 18, 17); steel 14 is excluded because its carbon

Table IV  
Slag Analyses Before Deoxidation

Steel No.	FeO	Fe <sub>2</sub> O <sub>3</sub>	MnO	Per Cent				
				SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	
<i>Rimmed Steels</i>								
2	17.78	10.10	8.87	9.32	2.07	43.12	6.25	1.21
18	23.15	12.85	7.64	6.40	1.56	40.66	6.00	0.82
<i>Semi-Killed Steels</i>								
4	14.15	10.08	12.37	12.80	2.46	37.80	9.72	1.06
<i>Silicon-Killed Steels</i>								
Ax	13.53	5.03	16.40	14.93	3.61	34.50	9.22	1.86
<i>Aluminum-Killed Steels</i>								
SMA-15	17.78	7.52	5.81	11.40	1.38	44.97	6.17	5.25
SMA-17	9.93	3.68	7.75	21.64	1.67	38.14	10.22	4.87
5	17.78	9.07	11.60	9.72	2.04	39.77	7.30	1.00
SMA-22	7.34	5.44	7.75	21.72	1.56	41.66	7.90	5.90
11	12.54	4.28	12.01	14.64	2.34	41.80	8.67	1.40

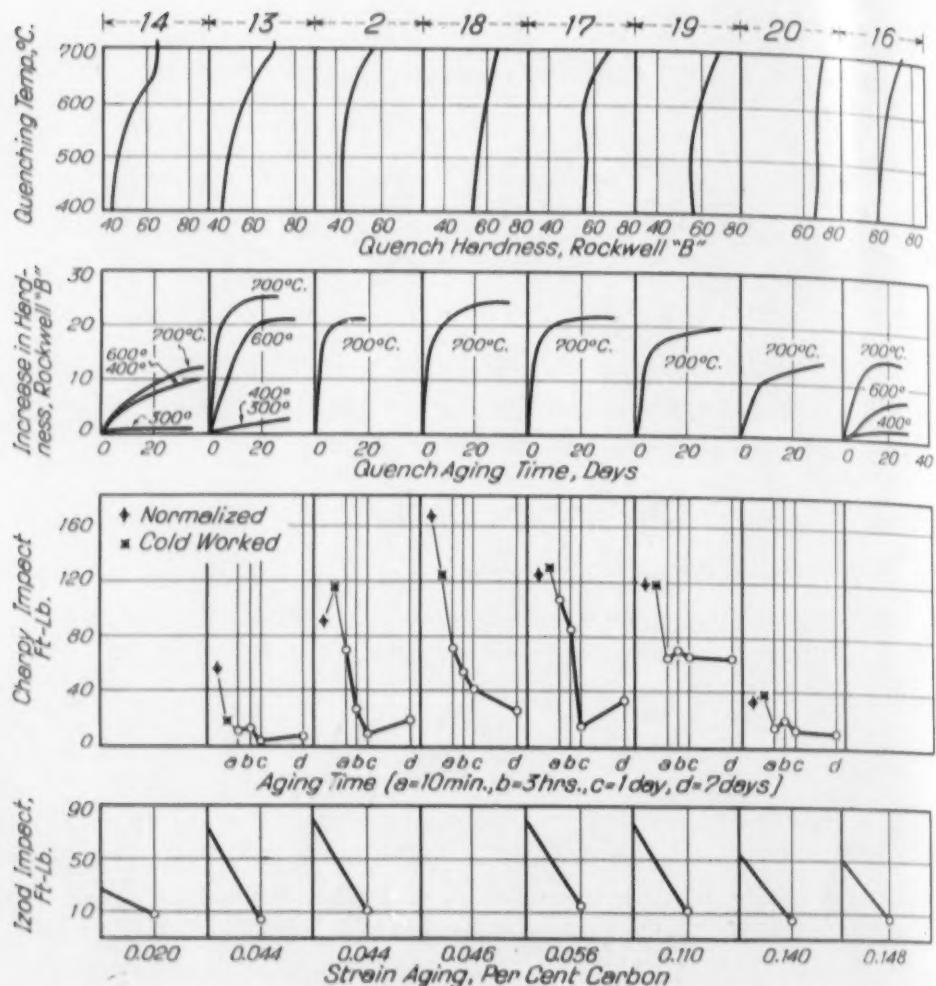


Fig. 2—Aging of Normalized Rimmed Steels.

content (0.020) is below the saturation concentration at 700 degrees Cent. (1290 degrees Fahr.) in the normalized or the quenched conditions were softer than the steels of higher carbon content; yet after the aging treatment the former became harder than the latter. In other words the hardness increase due to aging proper was greater in the former than in the latter, which may be interpreted as indicating that the ferrite in the quench-aged steels of lower carbon content became harder than in the higher carbon steels. From these facts it is logical to conclude that the decreasing aging with increasing carbon content is due to suppression of some precipitation effects, or an induced over-aging, rather than to the masking effect of the higher carbon on the increase in hardness.

Table V  
Quench-Aging. Rockwell "B" Hardness of Normalized, Quenched and Aged Steels

Steel No.	Carbon Per Cent	Rockwell Hardness			H*
		As Normalized	Quenched	"B" Scale Quenched and Aged	
<i>Rimmed Steels</i>					
14	0.0200	41.4	57.5	69.8	12.3
13	0.0440	45.1	62.6	87.9	25.3
2	0.0440	46.3	64.5	85.7	21.2
18	0.0466	51.0	67.0	91.2	24.2
17	0.0560	56.2	70.0	91.8	21.9
19	0.1100	55.9	69.9	89.8	19.9
20	0.1400	67.4	71.6	84.5	13.0
16	0.1480	60.3	66.6	81.2	14.6
<i>Semi-Killed Steels</i>					
7	0.094	55.2	67.1	85.2	18.1
8	0.150	61.9	72.2	82.1	9.9
K-7	0.154	70.4	71.9	78.0	6.6
4	0.192	70.0?	75.7	79.1	3.4
6	0.260	70.4	78.4	81.3	2.9
<i>Silicon-Killed Steels</i>					
I-46	0.040	....	70.9	83.1	12.2
I-44	0.042	....	67.7	77.9	10.2
I-56	0.170	....	76.6	80.0	3.4
AX	0.190	73.1	73.3	80.5	7.2
12	0.223	73.2	76.4	81.8	5.4
<i>Aluminum-Killed Steels</i>					
I-39	0.019	....	63.7	80.8	17.1
I-48	0.036	....	66.7	76.5	9.8
I-41	0.042	....	64.2	70.9	6.7
I-42	0.042	....	64.3	73.6	9.3
K-3	0.097	67.3	78.1	82.6	4.5
9	0.133	68.1	74.8	80.6	5.8
K-10	0.138	71.9	82.2	85.4	3.2
Izett	0.141	72.1	72.0	76.6	4.6
SMA-15	0.150	69.1	70.6	74.7	4.1
SMA-17	0.167	77.5	79.6	79.1	-0.5
I-52	0.167	....	72.0	71.6	-0.4
K-14	0.190	64.7	67.1	74.9	8.0
5	0.194	....	71.7	73.1	1.4
SMA-22	0.214	80.1?	87.9	86.9	-1.0
K-13	0.240	....	....	....	....
11	0.247	76.3	82.9	85.2	2.4

\*Increase in hardness due to aging.

(b) *Semi-killed Steels.* In Fig. 3 the semi-killed steels are shown to age considerably less than the rimmed steels, with the same general tendency for the aging to decrease with increasing carbon content. In these steels the oxygen content was lower than in the rimmed steels because they had been deoxidized to a greater degree.

(c) *Silicon-killed Steels.* As will be noted from Fig. 4, the silicon-killed steels showed considerable quench-aging, although this amounted to only about half as much as in the rimmed steels of the same carbon content. The amount of quench aging decreases with increasing carbon in the silicon-killed steels as also in the rimmed and the semi-killed steels.

(d) *Aluminum-killed Steels.* Figs. 5 and 6. Five electric furnace steels and 11 open-hearth steels were available in this group. In the aluminum-killed steels the effect of carbon on the quench aging was also noticeable, as shown in Figs. 5 and 6. In this type of steel the variation in dissolved oxygen content could not have been very great because all the steels contained an appreciable excess of aluminum,

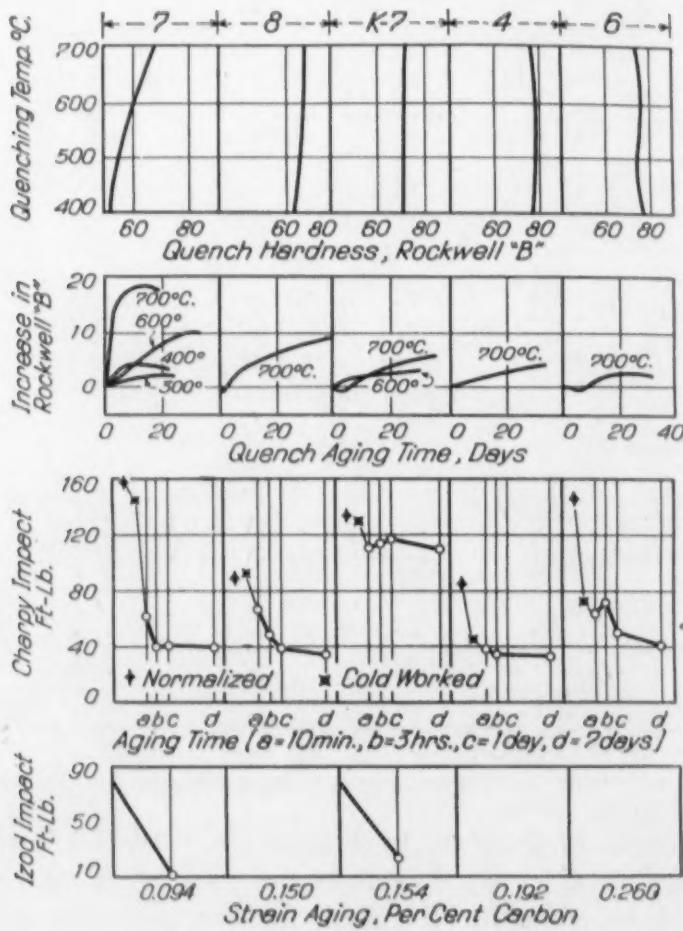


Fig. 3—Aging of Normalized Semi-killed Steels.

and thus oxygen could not have appreciably affected these results. Before deoxidation, the lower carbon steels in this group contained more oxygen than the higher carbon steels, and it is possible that the type of suspended nonmetallic material was quite different in the finished steel as the carbon increased.

The data on the effect of carbon content and deoxidation on quench aging are summarized in Fig. 7.

A few steels were tested for aging after quenching from 600, 500, 400 and 300 degrees Cent. (1110, 930, 750, 570 degrees Fahr.). The results given in Figs. 2, 3, 4 and 6, show that as the quenching temperature decreased the degree of hardening upon aging decreased.

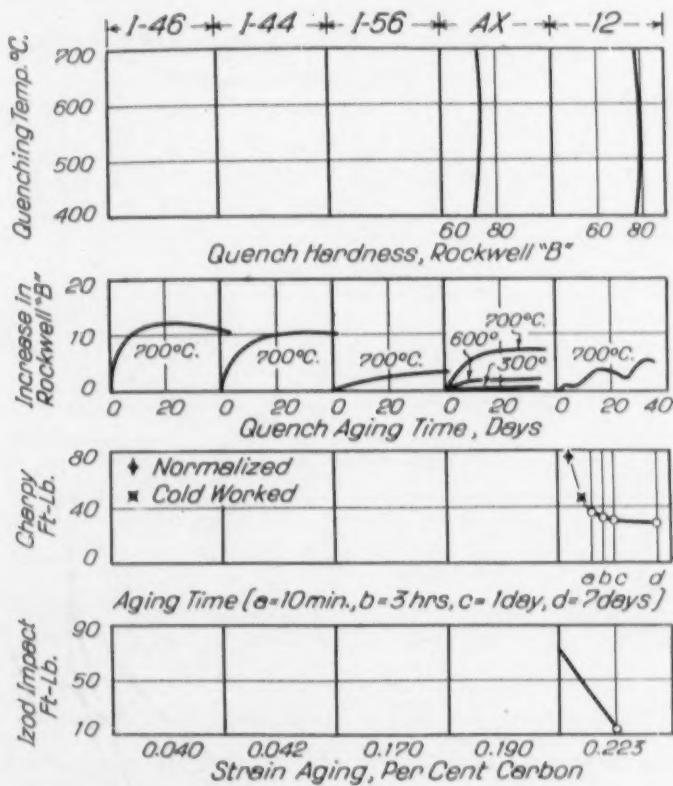


Fig. 4—Aging of Normalized Silicon-killed Steels.

This will be discussed in the next section dealing with the results of quench hardness experiments.

#### Quench Hardness

In order to determine whether or not the steels which showed the greater aging after quenching also showed the greater increase in hardness with increasing quenching temperature, samples were quenched from various temperatures from 400 to 715 degrees Cent. (750-1320 degrees Fahr.), and hardness readings were taken immediately. The results, summarized in Figs. 2 to 6, indicate that the hardness increase with rising temperature in the rimmed steels is considerable, while in some of the killed steels it becomes practically independent of the temperature of quenching.

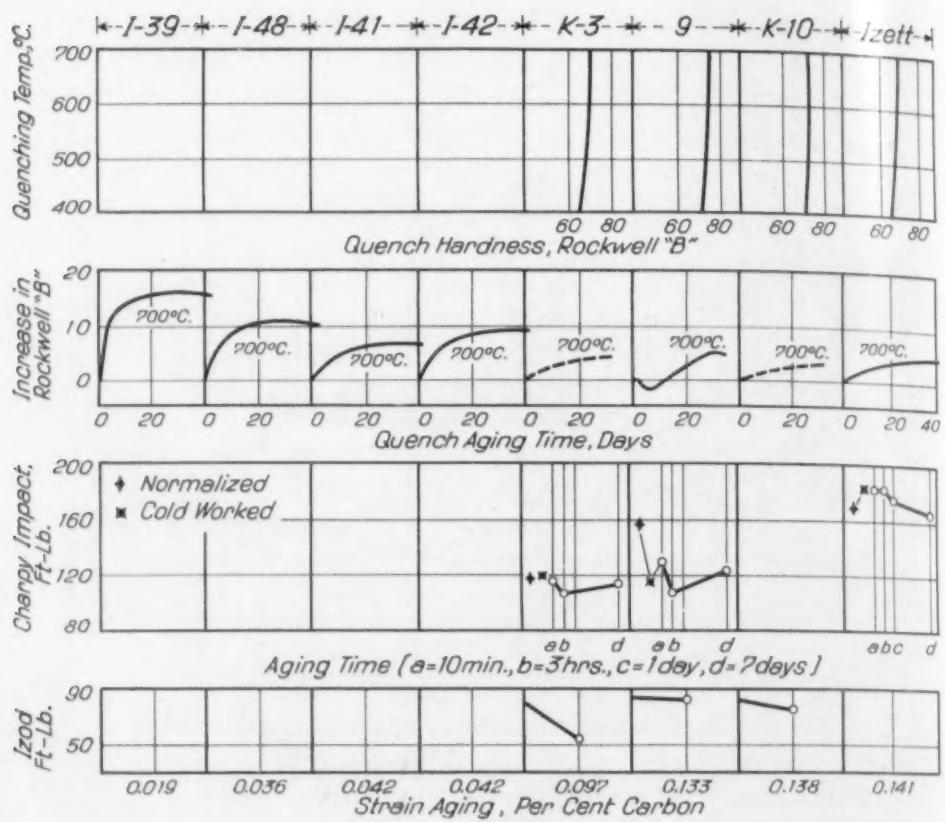


Fig. 5.—Aging of Normalized Aluminum-killed Steels.

From the consideration of the above data, it might be assumed that the shape of the solid solubility line may vary with the following three factors: (1) carbon content of the steel, (2) oxygen content, and (3) changing type of suspended nonmetallic material. Consequently, it seems logical to assume that varying amounts of carbon may be found dissolved in ferrite at a given temperature depending on the presence of oxygen in solution, and on the type of nonmetallic matter. These two factors are determined by variations in melting and deoxidation practice, and may affect the amount of dissolved carbon either by actually changing its solubility, or by changing the rate of its diffusion.

The evidence in favor of the above views is the fact that the greater hardening with rising quenching temperature is accompanied by greater hardening upon aging. Comparison of steels with the same carbon content but deoxidized to various degrees will show that the killed steels age less than the rimmed steels. As an illustration,

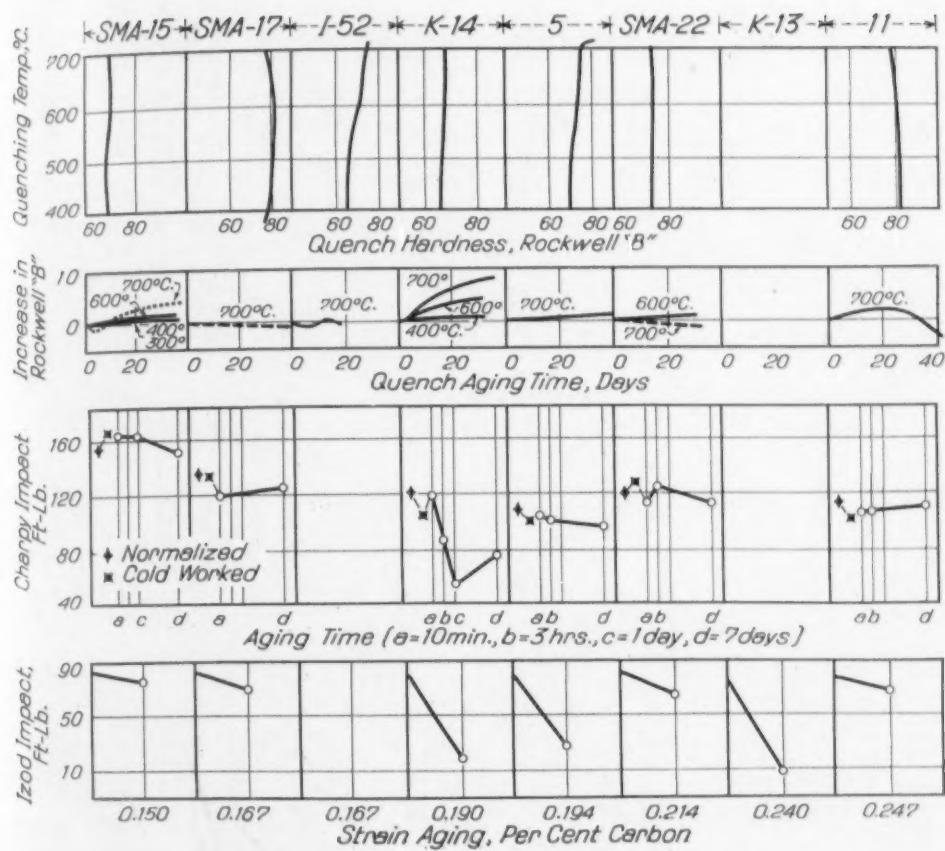


Fig. 6—Aging of Normalized Aluminum-killed Steels.

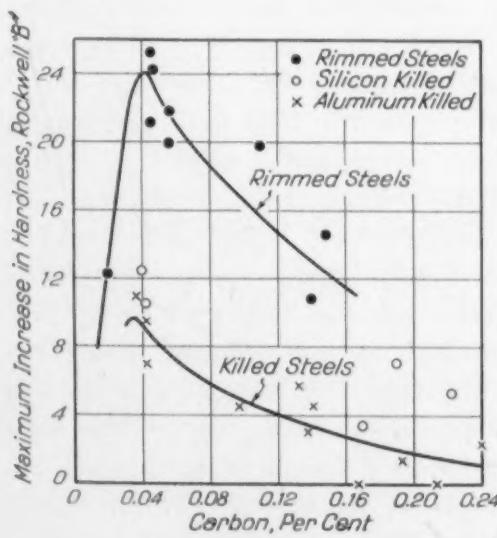


Fig. 7—Effect of Carbon Content and Deoxidation on Quench-Aging of Steel.

rimmed steel No. 16 showed an increase in hardness of 14 points whereas the increase in steel SMA-15, aluminum-treated, was only 4 points. The carbon content of the two steels is nearly the same, and the difference in aging, therefore, may be due either to the lower oxygen content of the aluminum-treated steel SMA-15 or to the finer grain-size; or it may be due to the presence of the finely dispersed alumina particles.

#### OVER-STRAIN AGING

##### *Normalized Steels—Impact Specimens Compressed 2 Per Cent, Aged at 100 Degrees Cent., and Tested at 21 Degrees Cent.*

The results of these tests are given in Figs. 2 to 6.

(a) *Rimmed Steels.* As Fig. 2 indicates, the drop in impact strength in all rimmed steels is great, the maximum aging occurring in the steels with about 0.05 per cent carbon.

(b) *Semi-killed and Silicon-killed Steels.* In these grades of steel the aging is much less pronounced than in the rimmed steels, and the amount of aging decreases as the carbon content increases (Figs. 3 and 4).

(c) *Aluminum-killed Steels.* Generally, these steels age little, some of them being practically non-aging. Arranging the steels in the order of increased carbon content, as in Figs. 5 and 6, does not bring out any definite relation between the carbon content, and the susceptibility to over-strain aging. It will be noted, however, that the carbon content of these steels is comparatively high, the lowest carbon being 0.097 per cent in steel K-3, which is far above the concentrations at which carbon has a pronounced effect on over-strain aging (0.05 per cent). Furthermore, the data are not as consistent as the impact data for rimmed or semi-killed steels. This is not due to any inherent lack of uniformity of these steels, but mainly to the unfortunate circumstance that the capacity of the impact machine (120 foot-pounds) was not sufficient to break some of these steels. Consequently, all the values above 120 foot-pounds are only rough approximations, obtained by adding to 120 the values that were obtained on breaking the specimens which were only bent in the first blow of the hammer. However, the examination of all the data, both above and below 120 foot-pounds, and comparison to the values obtained on the other three grades of steels indicates clearly that the

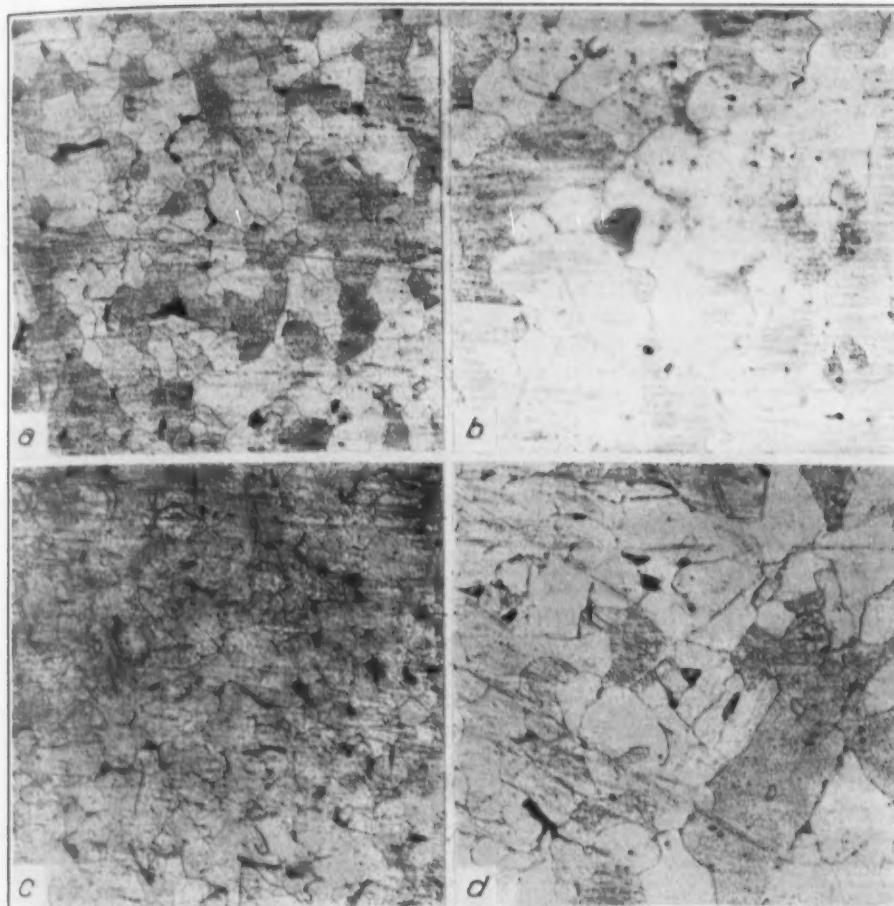


Fig. 8—Grain-Size of Rimmed Steels.  $\times 100$ . a. Steel 24, Normalized; b. Steel 24, Air-cooled from 1100 Degrees Cent.; c. Steel 66, Normalized; d. Steel 66, Air-cooled from 1100 Degrees Cent.

aluminum-treated steels are far less susceptible to over-strain aging than the other steels. All the steels maintained high impact values upon the aging treatment with the exception of steel K-14 which showed a marked drop in impact. This steel was deoxidized with manganese in the furnace and aluminum in the ladle, and no silicon was added. The incomplete deoxidation of this steel, or the resulting coarser structure as compared to other aluminum-killed steels, may account for the marked tendency of this steel to age.

A summary of the influence of deoxidation on the strain aging of steels is given by the figures below which represent the average decrease in the impact strength in the four groups of the steels:

Type of Steel	Average Decrease in Impact Strength, Foot-Pounds
Rimmed	74
Semi-killed	47
Silicon-killed	19
Aluminum-treated	12

**Hardness Tests.** Hardness tests made on the compressed portions of the impact specimens appear to be of little value, first, because of the large scatter of individual results in some of the steels,

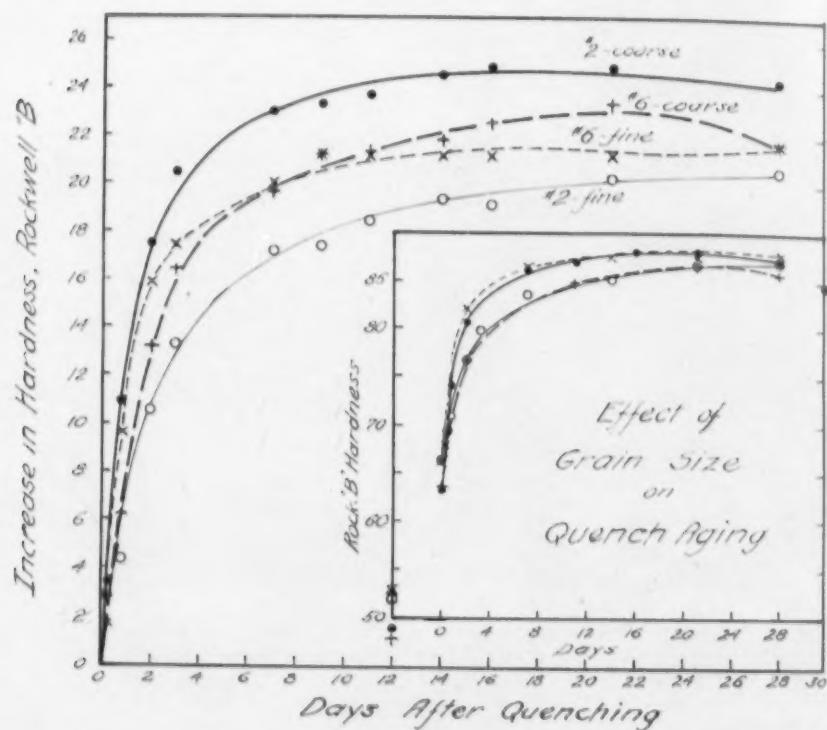


Fig. 9.—Effect of Grain-Size on Hardness Tests in Quench Aging of Rimmed Steels.

and second, because in most of the steels they failed to reflect the course of the age hardening.

**Tensile Tests.** It is well known that the break at the yield point in the stress-strain diagrams obtained in the tensile test disappears when the steel is quenched from about 700 degrees Cent. (1290 degrees Fahr.) or cold-worked, and reappears after an aging treatment. The reappearance of the yield point and the amount of the yield-point elongation are considered by many as the best test for determining the aging characteristics of steel intended for fabrica-

tion involving considerable amount of deformation, such as encountered in the deep drawing of sheets.<sup>69, 70, 71</sup>

A few tensile tests were made with the purpose of ascertaining the superior immunity of the aluminum-killed steels to aging in comparison to other steels, and likewise to obtain some data on the tensile characteristics of these steels. The three aluminum-treated steels (SMA-15, SMA-17, and SMA-22) and a semi-killed steel K-7 were selected for these tests. The steels were normalized, and three or four specimens of each steel were prepared. In each steel, one specimen of standard size was tested in the "as-normalized" condition. The other three were machined to 0.517 inch diameter and pulled to 0.505 inch diameter, whereby a 2.3 per cent reduction in diameter (or a 5 per cent reduction of area) was obtained. Of these, one was tested immediately, one after 1 day's aging, and one after 5 days' aging at 100 degrees Cent. Complete stress-strain diagrams were obtained on all specimens. The data on the tensile properties are given in Table VI. In the "as-normalized" condition all the steels showed a pronounced yield point accompanied by considerable elongation at constant load. After cold-working only a slight break indicating the yield point remained in the curves for all the steels; a slight "yield point elongation" persisted in the semi-killed steel K-7 and in the aluminum-treated steel SMA-15. In the other two aluminum-treated steels the yield point elongation was practically eliminated by the cold deformation.

Aging subsequent to cold-working resulted in an almost complete recovery of the yield point in the silicon-killed steel K-7, and in partial recovery in the aluminum-treated steels SMA-15 and SMA-17, the yield point elongation amounting to about one quarter of the original elongation of the normalized steels. In steel SMA-22 the strain-aging treatment failed to restore the yield point elongation, indicating that this steel is practically free from aging. The results are in good agreement with the data obtained in impact tests, and confirm the beneficial effect of deoxidation in preventing the aging in steels.

The tensile strength, the elongation, and the reduction of area of the three SMA steels investigated do not appear to be much influ-

<sup>69</sup>Ref. 58.

<sup>70</sup>Ref. 10.

<sup>71</sup>R. O. Griffis, R. L. Kenyon and S. Burns, "The Aging of Mild Steel Sheets," Year Book American Iron and Steel Institute, 1933.

Table VI  
Over-Strain Aging. Tensile Tests

Treatment	Upper	Lower	Maximum	Elonga-	Reduc-	Elongation at	
	Yield	Yield	Tensile			Yield Point	
	Strength	Strength	Strength	Per Cent	Per Cent	In 2 In.	Per Cent
<i>Steel K-7—Semi-Killed</i>							
As normalized .....	39400	32500	56000	45.0	66.4	0.032	1.60
Cold worked .....	43100		58450	40.5	66.2	0.003	0.15
Cold worked and aged 5 days at 100° C. ....	58250	55800	63250	30.7	64.8	0.028	1.40
<i>Steel SMA-15</i>							
As normalized .....	35850	34850	57000	45.5	71.7	0.042	2.10
As cold-worked .....	46300	.....	59000	38.0	72.8	0.002	0.10
Cold worked and aged 1 day at 100° C. ....	50000	49600	60230	39.0	71.9	0.012	0.60
Cold worked and aged 5 days at 100° C. ....	51000	50650	59750	43.0	71.9	0.010	0.50
<i>Steel SMA-17</i>							
As cold worked .....	54800	.....	68320	35.5	62.0	0.000	0.00
Cold worked and aged 1 day at 100° C. ....	60950	60300	66150	34.0	68.2	0.010	0.50
Cold worked and aged 5 days at 100° C. ....	58000	57400	67000	37.5	67.2	0.009	0.45
<i>Steel SMA-22</i>							
As normalized .....	40000	38150	64000	39.0	66.5	0.028	1.40
As cold worked .....	54400	.....	67250	38.0	65.2	0.000	0.00
Cold worked and aged 1 day at 100° C. ....	55850	.....	67300	38.5	64.1	0.004	0.20
Cold worked and aged 5 days at 100° C. ....	58000	.....	68200	37.0	64.0	0.000	0.00

enced by aging. The yield strength increases considerably both as the result of cold-working and of aging. In the semi-killed steel K-7, the reduction of area is little affected, but the elongation decreases considerably, and the tensile strength, and particularly the yield strength increase noticeably.

The tests made on Izod impact specimens which had been compressed 15 per cent, aged 5 minutes at 450 degrees Cent. (840 degrees Fahr.) and 1 day at room temperature, have been reported<sup>12</sup> in Cooperative Bulletin 66 and the results are presented here for the sake of completeness (Figs. 2 to 6). It has been reported that all the rimmed, semi-killed and silicon-killed steels investigated showed a marked drop in impact resistance when subjected to the above treatment. The average percentage decrease in impact values for the three classes of steel is as follows:

Rimmed .....	86
Semi-killed .....	78
Silicon-killed .....	80

<sup>12</sup>C. H. Herty, Jr., and B. N. Daniloff, "The Effect of Deoxidation on the Aging of Mild Steel," Cooperative Bulletin 66, Carnegie Institute of Technology, 1934.

In the aluminum-killed steels, those with the strongest deoxidation showed the least drop in the impact. It was also reported that the three SMA steels had shown higher impact values than other aluminum-killed and semi-killed steels, though in the as-rolled condition all the steels were far more susceptible to the effect of straining and aging at 450 degrees Cent. (840 degrees Fahr.) than in the normalized condition; normalized steels gave much higher impact values after straining and aging at room temperature than the as-rolled material.

#### *Over-strain Aging of Normalized Box-annealed Aluminum-killed Steels*

In order to ascertain whether or not a treatment at sub-critical temperatures might alter the capacity of these steels to age, specimens of the three aluminum-killed steels, SMA-15, SMA-17 and SMA-22, were normalized, then heated to 1150 and 1300 degrees Fahr. (620-705 degrees Cent.), held at these temperatures for 24 hours and cooled slowly in the furnace. The cooling rate was retarded so as to allow four days for the cooling to room temperatures. Charpy impact specimens were made and tested after compressing 2 per cent and aging at 100 degrees Cent. for various periods of time.

In Table VII the impact and hardness values are tabulated together with those previously obtained on the normalized specimens for comparison. The box-annealing treatment resulted in the softening of the steels with corresponding increase in the impact resistance which persisted upon the aging treatment.

Steel SMA-15 which had been box-annealed at 1150 and 1300 degrees Fahr. showed no hardening upon aging for a period of 1 day at 100 degrees Cent.; on the 7th day, however, it hardened somewhat, although it still was considerably softer than the normalized steel aged for the same length of time.

Cold-working the box-annealed steels SMA-17 and SMA-22 resulted in considerable increase in hardness (although this hardening is not reflected in the impact data); subsequent aging produced no further change in the hardness of the steels.

It is concluded from these limited data that the combined result of box-annealing and over-strain aging treatments is a slightly softer and tougher steel as compared to the normalized and strain-aged steel. This softening is, however, due mainly to the effect of the

Table VII  
Over-Strain Aging Tests of Normalized, and Normalized and Box-Annealed SMA Steels

Treatment	Charpy Impact, Ft.-Lb.*		Hardness, Rockwell "B"†			
	Box-Annealed from 1150° F.	Box-Annealed from 1300° F.	Normalized	Box-Annealed from 1150° F.	Box-Annealed from 1300° F.	
<i>Steel SMA-15</i>						
As cooled . . . . .	153	179	174	71.8	65.5	62.1
Cold worked . . . . .	168	200	169	73.9	65.8	63.3
Cold worked and aged 10 min. . . . .	163	196	163	71.1	66.3	64.0
Cold worked and aged 3 hours . . . . .	191	197	197	72.3	65.8	63.3
Cold worked and aged 24 hours . . . . .	162	200	170	72.3	63.1	59.1
Cold worked and aged 7 days . . . . .	148	179	192	73.5	68.4	67.5
<i>Steel SMA-17</i>						
As cooled . . . . .	134	165	140	76.7	72.2	66.3
Cold worked . . . . .	135	128	161*	78.3	74.0	71.1
Cold worked and aged 10 min. . . . .	119	141	167	76.1	73.4	71.8
Cold worked and aged 3 hours . . . . .	127	151	143	74.9	73.7	68.8
Cold worked and aged 24 hours . . . . .	123	144	170	76.8	73.7	70.8
Cold worked and aged 7 days . . . . .	123	142	140	76.2	75.4	71.9
<i>Steel SMA-22</i>						
As cooled . . . . .	119	130	125	77.7	72.3	66.2
Cold worked . . . . .	127	145	126	77.9	74.3	70.1
Cold worked and aged 10 min. . . . .	112	158	117	78.8	72.9	69.4
Cold worked and aged 3 hours . . . . .	124	155	156	78.6	73.2	69.3
Cold worked and aged 24 hours . . . . .	101	161	138	76.6	73.8	68.5
Cold worked and aged 7 days . . . . .	111	126	127	77.4	74.4	69.8

\*Average of 2 tests.

†Average of 4 tests.

annealing treatment; the results of the strain-aging treatment proper appear to be little affected by the box-annealing treatment employed in these tests on the steels selected for study.

#### EFFECT OF GRAIN-SIZE ON THE AGING OF STEEL

It is a well known fact that aluminum when used as a deoxidizer produces fine grain in steel. As the aluminum-treated steels age less than steels of similar chemical composition not treated with aluminum, the question arises as to whether the fine grain-size of these steels may not be the major factor responsible for the non-aging properties of these steels, rather than their freedom from dissolved oxygen. As mentioned in the discussion of the work of others, there is no conclusive evidence regarding the influence of grain-size; a few statements found in the literature are quite contradictory.

No attempt was made in this work to investigate fully the effect of grain-size on aging in view of the large amount of time and work that would be required for a comprehensive study of the subject.

However, two sets of tests were made in order to determine how extremes in grain-size affect the quench- and over-strain aging.

For these tests two rimmed steels, No. 24 and 66, containing 0.040 and 0.060 per cent carbon respectively, were used. The coarse grain in these steels was obtained by heating at 1100 degrees Cent. (2010 degrees Fahr.) and cooling in air. The grain-size of the coarse- and fine-grained (normalized) steels is shown in Fig. 8.

*Quench Aging Tests.* The results of hardness tests made on specimens quenched from 700 degrees Cent. (1290 degrees Fahr.) and aged at room temperature are given in Fig. 9. It will be seen that in steel 24 the grain-coarsening treatment has resulted in considerable increase in aging, while in steel 66 aging seems to be practically independent of the grain-size.

The results obtained on a limited number of impact tests made on quench-aged specimens are given in Fig. 10. These data indicate that the final impact values after aging are slightly higher in the fine-grained steels than in the coarse-grained. However, the fine-grained steels possessed a much higher original impact resistance in the freshly quenched state than the coarse-grained, and, therefore, the actual decrease in impact (or percentage drop) due to aging proper is greater in the fine- than in the coarse-grained steels.

*Strain Aging Tests.* The steels were cold-worked by compressing so as to reduce the thickness of the samples by 5 per cent. This treatment reduced the impact resistance of both steels to very low values as shown in Fig. 10. Subsequent aging lowered the impact of this fine-grained steel still further, but had little effect on the coarse-grained steel. The actual values were somewhat higher in the fine-grained steel, although the drop (actual or percentage) was greater because the original strength (as normalized) was much higher in the fine-grained steels.

To determine whether or not an aluminum-killed steel (which is practically non-aging when tested for strain aging after normalizing) will become more susceptible to aging in the coarse-grained condition, steel SMA-15 was heated for  $\frac{1}{2}$  hour at 1100 degrees Cent. (2010 degrees Fahr.) and cooled in air. Rimmed steel No. 19, containing 0.110 per cent carbon, was selected for comparison tests. This steel was subjected to the similar grain-coarsening treatment as SMA-15. The grain-size of both steels resulting from the treatment, together with the grain-size of the normalized steels is shown in Fig. 11. Impact specimens were compressed 2 per cent

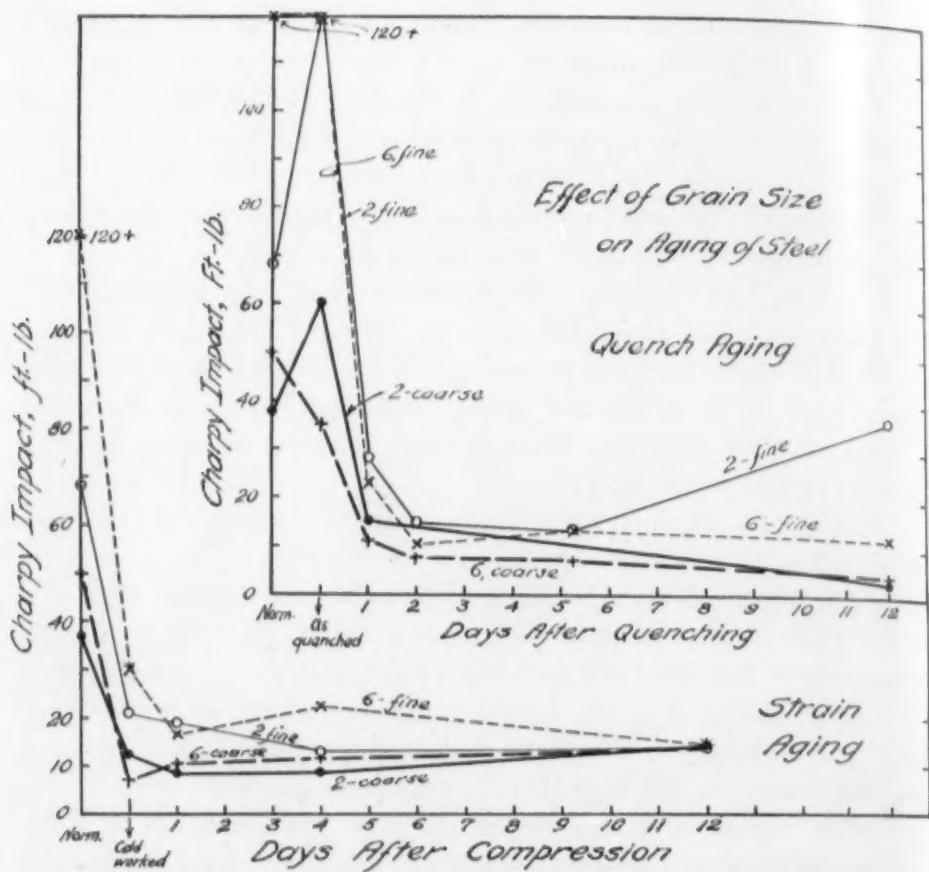


Fig. 10—Effect of Grain-Size on Impact Tests in Quench and Over-strain Aging of Rimmed Steels.

and subjected to aging at 100 degrees Cent. for various periods of time.

As may be seen from the hardness data in Fig. 12, the fine-grained SMA-15 steel is practically non-aging, while in the coarse-grained condition an increase in hardness of about 3 points has resulted. The rimmed steel No. 19 aged considerably more in the coarse-grained condition than in the fine-grained.

Incidentally, it will be noted that the hardening effect of cold-working alone is much greater in the rimmed than in the SMA steel. In both steels the hardening effects of the cold-working and of the aging treatment proper and consequently the total effect of the overstrain aging treatment are greater in the coarse-grained condition than in the fine-grained.

Comparison of the two steels will show that grain growth enhances the aging in the aluminum-treated steel but the degree of hard-

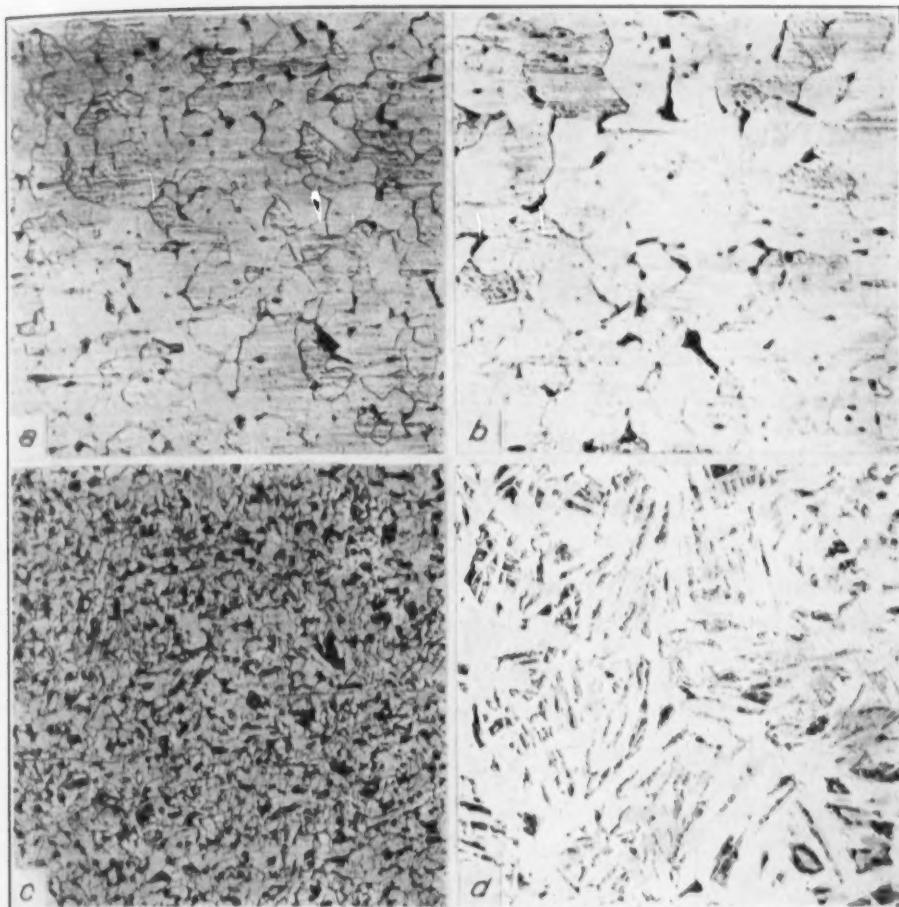


Fig. 11—Grain-Size of Steels 19 and SMA-15.  $\times 100$ . a. Steel 19, Normalized; b. Steel 19, Air-cooled from 1100 Degrees Cent.; c. Steel SMA-15, Normalized; d. Steel SMA-15, Air-cooled from 1100 Degrees Cent.

coarsening is of far lesser magnitude, and that in the coarse-grained condition the aluminum-treated steel ages less than the rimmed steel in the fine-grained condition. Reference to Fig. 11 will indicate that the coarse grain produced in the SMA steel is much coarser than the fine grain in the rimmed steel; yet the rimmed steel ages more. It is inferred from this that although the fineness of grain of the aluminum-treated steels used in this investigation undoubtedly contributes to their low susceptibility to aging, the effect of the grain-size is only a minor one as compared to the major effect of the variations in dissolved oxygen content.

The results of the impact tests are in complete agreement with those obtained by hardness measurements. The grain-coarsening

Table VIII  
Influence of Grain-Size on Over-Strain Aging Impact Tests

Treatment	Grain Size	Charpy Impact, Ft.-Lb.			
		Steel #19 Normalized from 900°C. Fine	Air Cooled from 1100°C. Coarse	Steel SMA-15 Normalized from 900°C. Fine	Air Cooled from 1100°C. Coarse
As cooled		119.0	41.7	150.0	146.0
Cold worked		120.0	18.4	167.0	138.0
Cold worked and aged 10 min.		65.5	20.6	163.0	85.0
Cold worked and aged 1 hour			12.0	....	53.0
Cold worked and aged 3 hours		72.1	12.1	....	....
Cold worked and aged 24 hours		46.5	9.6	162.0	99.0
Cold worked and aged 7 days		65.3	9.9	148.0	74.0
Per cent drop in impact due to cold working		0	56.0	....	5.5
Per cent drop in impact due to aging		45.7	46.2	11.3	46.0
Total per cent drop in impact		45.5	76.3	11.3	49.0
Actual decrease in impact due to cold work		....	23.3	....	8.0
Actual decrease in impact due to aging		55.0	8.5	....	64.0
Total decrease in impact		55.0	31.8	15.0	72.0

treatment alone resulted in considerable embrittlement of the rimmed steel, while in the aluminum-treated steel the effect was only slight. Cold-working did not lower the impact strength of either steel in the fine-grained condition; in the coarse-grained condition the rimmed steel was embrittled considerably, while the aluminum-treated steel only slightly.

If the relative drop in impact be expressed as the percentage drop due to each of the components of the strain-aging treatment, namely, the cold-working, and the aging proper (Table VIII), it will be noted that in both steels in the fine-grained condition practically all of the embrittlement is due to the aging treatment proper. In the coarse-grained condition, the major embrittling factor was cold working for the rimmed steel, and aging for the aluminum-treated steel.

In Fig. 13 the impact data are plotted and smooth lines drawn, very roughly, because of the considerable scatter of individual points. Because of the large differences in the toughness of these four steels the lines are accurate enough to show the superior toughness of the aluminum-treated steel (a fact which has been known for many years). The grain-coarsening heat treatment, indeed, destroys its non-aging properties, and considerable embrittlement ensues. Yet, a glance at Fig. 13 will show that the strain aging curve of the SMA steel in the coarse-grained condition roughly coincides with the curve for the rimmed steel in the fine-grained condition.

It will be remembered that the average coarse grain of steel SMA-15 referred to is much larger than that of the fine-grained

rimmed steel 19 (curves II and III in Fig. 13). As shown in Fig. 11, in the normalized condition the variation in grain-size of the two steels is slight compared to the exaggerated difference of grain-size in the steels represented in curves II and III. In other words, in these tests, only extremes in grain-size were tested, and from the fact that a very large grain had to be developed in the aluminum-treated steel in order to render it as susceptible to over-strain aging as a fine-grained rimmed steel, it is inferred that a

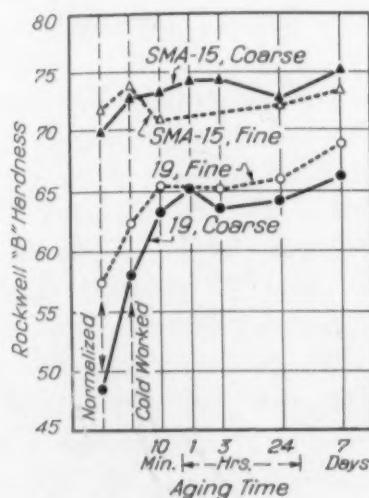


Fig. 12—(Left) Effect of Grain-Size on Over-strain Aging of Rimmed and Aluminum-treated Steels.

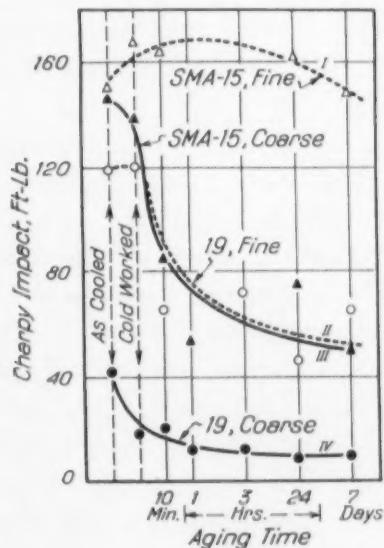


Fig. 13—(Right) Effect of Grain-Size and Deoxidation on Strain Aging.

grain-size equal to that of a normalized rimmed steel would not result in any great embrittling effect, and the aluminum-treated steel would still be less susceptible to aging than the rimmed steel.

An examination of Figs. 12 and 13 and photomicrographs in Fig. 11 will indicate that grain-size affects the impact resistance to a much greater extent than the hardness, although both hardness and impact tests indicate conclusively that grain-size is an important factor determining the aging properties of steel.

There is no doubt that, as measured by the hardness tests, coarse-grained steels are more susceptible to aging, both after quenching and after cold-working, than fine-grained steels. The grain-coarsening treatment resulted in a great lowering of impact resistance of the steels both after quench and after over-strain aging.

The above statements refer to the total aging effect, i.e., the

combined effect of either quenching and aging, or cold-working and aging. It must be emphasized here that the relative amounts of embrittlement due to either one of these two component effects vary with the grain-size and with the degree of deoxidation. Grain-coarsening treatment lowers the impact and decreases the hardness of rimmed steels considerably, and affects the aluminum-treated steel only slightly. Cold-working (2 per cent) has little effect on fine-grained steels, causes brittleness in coarse-grained rimmed steel, and has only a slight effect on the coarse-grained SMA steel. Aluminum-treated steel with artificially produced coarse grain aged considerably; in the fine-grained condition this steel was practically non-aging.

It may thus be inferred that the fine grain-size of the aluminum-treated steels is, undoubtedly partly responsible for their low susceptibility to aging, but a consideration of the grain-size of the steels of various degrees of deoxidation indicates that the fine grain-size is only one, and possibly a minor factor contributing to the non-aging properties of the aluminum-killed steels. This conclusion is in contradiction with the generally observed fact that rates of reactions are faster in fine-grained than in coarse-grained materials. Inasmuch as the steels were heated at 1100 degrees Cent. (2010 degrees Fahr.) it is possible that appreciable amounts of oxygen have been absorbed during this treatment, and the increased tendency of coarse-grained steels to age may be due to oxide precipitation. If repetition of the above tests using a neutral atmosphere should show this to be true, the above conclusion is subject to change.

#### AGING AT ELEVATED TEMPERATURES

Köster<sup>73</sup> has shown that carbon and nitrogen may precipitate from ferrite independently of each other. By plotting the variations in coercive force with the temperature of aging he obtained separate maxima on the curves, one interpreted as due to the precipitation of the nitrogen (150 degrees Cent.) and the other to that of carbon (300 degrees Cent.). Similar curves were obtained by Buchholtz and Köster<sup>74</sup> on a copper steel, where the curves representing variations in hardness with aging temperature showed two peaks, one at-

<sup>73</sup>Ref. 36.

<sup>74</sup>H. Buchholtz and W. Köster, "Ueber die Anlasshärzung Kupferlegierten Stahler," *Stahl und Eisen*, Vol. 50, 1930, p. 687-695; disc. *ibid.* pp. 997-999.

tributed to the precipitation of carbon and the other to the precipitation of copper.

Quench and the over-strain aging at elevated temperatures were investigated using three rimmed and one aluminum-treated steel. Aging curves were obtained for various temperatures varying from room temperature to 300 degrees Cent. (570 degrees Fahr.), and as a corollary it was attempted to discriminate between the effects of carbon and oxygen on the aging by plotting hardness increase vs. aging temperature for various periods of time.

*Over-strain Aging Tests.* For these tests three rimmed steels were selected with varying carbon and varying oxygen content:

Steel	Carbon, Per Cent	FeO, Per Cent
20	0.140	0.027
16	0.148	0.046
17	0.056	0.046

Specimens of these steels were normalized in a nitrogen atmosphere, ground to predetermined thickness and cold-worked by compressing in a die so as to reduce the thickness by 7 per cent. Hardness tests were made before and immediately after cold working. The specimens were then heated at various temperatures and hardness tests made after heating for various times.

Plotting increase in hardness against aging temperature (Fig. 14), though giving some hints of a second maximum, failed to give evidence on the point. It is quite possible that the suggestions of the second peaks are manifestations of the precipitation of oxygen. Possibly the two processes, the coagulation of carbide and the precipitation of oxide overlap each other and as a result no distinct sharply defined minima or maxima are produced.

*Quench-Aging.* The above experiments were repeated on specimens given a quench-aging treatment. For these tests rimmed steels 17 and 20, and the aluminum-treated steel SMA-15 were used. The latter is a low oxygen steel, and it was desired to test it in order to see whether or not the absence of oxygen would be reflected in the shape of the hardness-aging temperature curves.

The specimens were normalized in a nitrogen atmosphere, then heated for 1 hour in a nitrogen atmosphere at 700 degrees Cent. (1290 degrees Fahr.), and finally quenched in water. In Fig. 15 the increase in hardness due to aging is plotted against the aging temperature for various periods of time. The curves show one

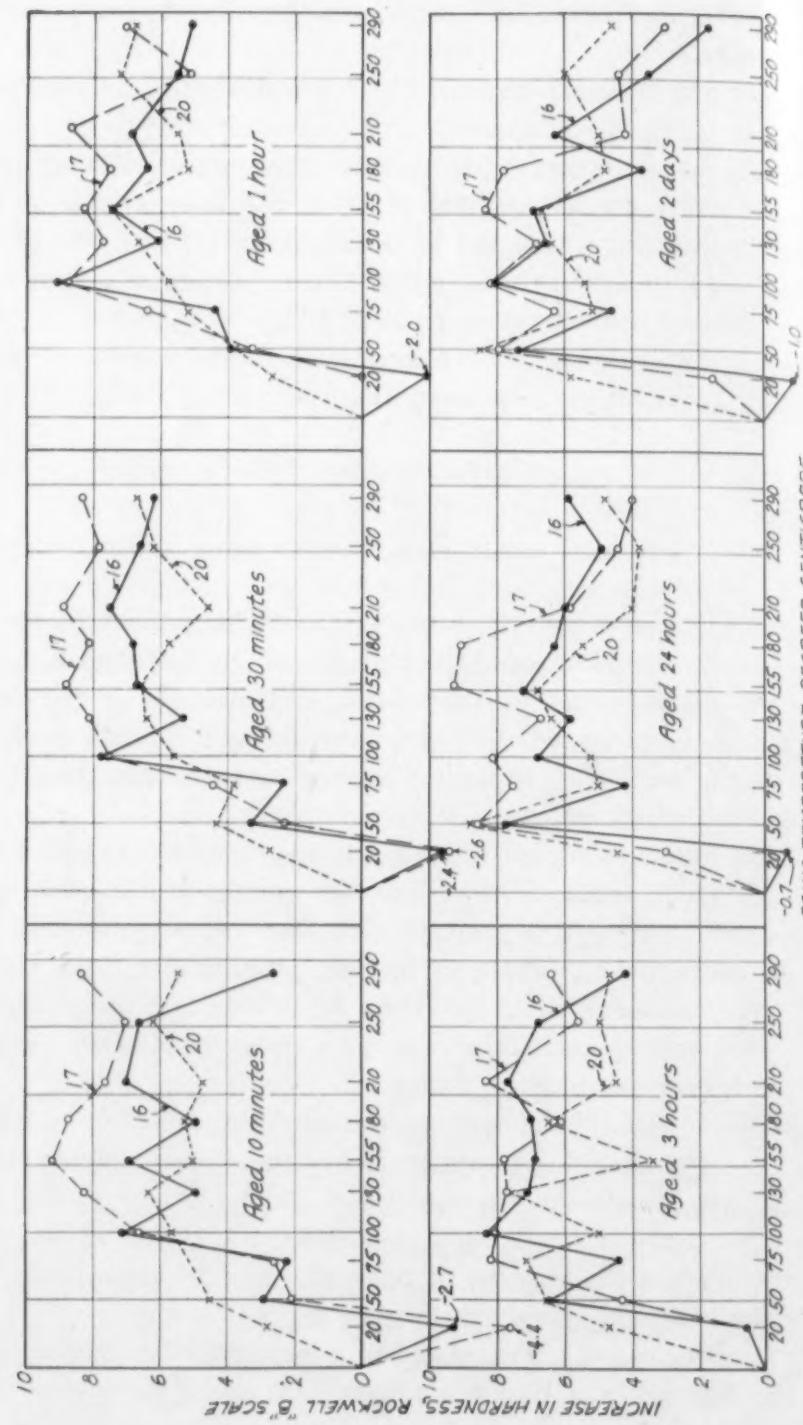


Fig. 14—Over-strain Aging of Rimmed Steels at Elevated Temperatures.

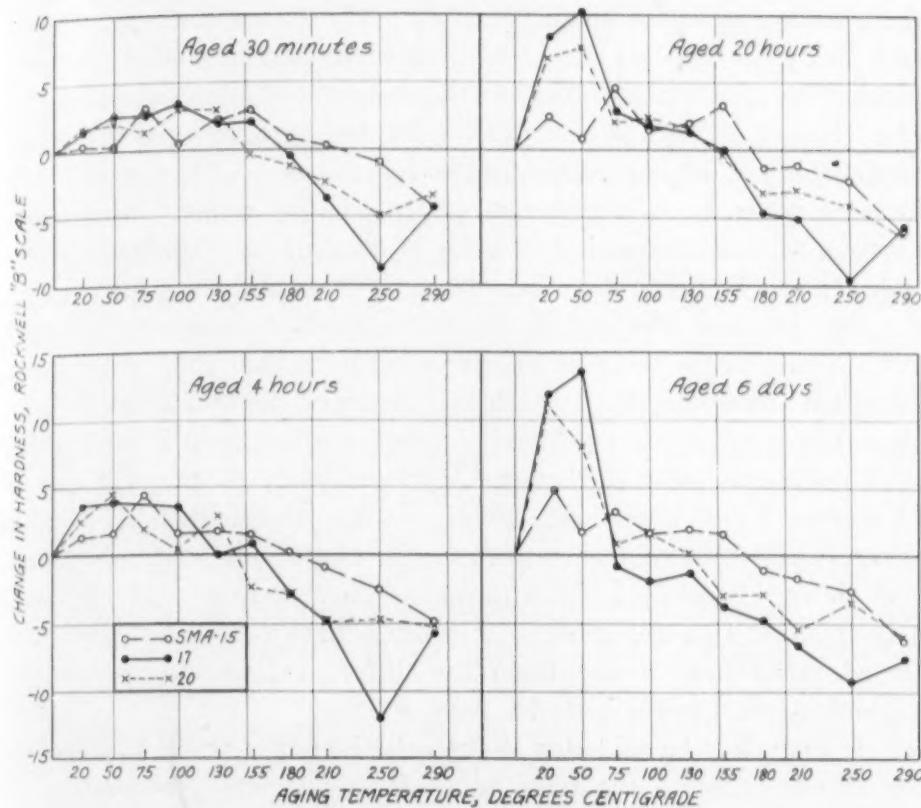


Fig. 15—Quench Aging of Rimmed and Aluminum-treated Steels at Elevated Temperatures.

aging. No second maxima of comparable magnitude appear; small peaks on some of the curves are apparently due to experimental error. Some softening occurred in the rimmed steel No. 17 upon aging at 250 degrees Cent. (480 degrees Fahr.) which was followed by hardening upon aging at 290 degrees Cent. (555 degrees Fahr.). It is possible that a second peak would appear in this steel upon aging at still higher temperatures; however, no attempt was made to determine this, owing to the lack of time.

#### INFLUENCE OF DEOXIDATION ON THE RATE OF AGING

Although the above tests failed to demonstrate the precipitation of oxygen, the curves, nevertheless, are of interest since they give an insight into the rates of precipitation and of coagulation of the precipitated materials. Comparison of the curves in Fig. 15 will show that at lower temperatures the rimmed steels aged much faster than

the aluminum-treated steel SMA-15. The latter steel lags behind and the peak appears at higher temperatures, and only on long heating (6 days) is it shifted to the same low temperature as in the two rimmed steels. Correspondingly, the softening in the SMA steel begins at higher temperatures for the same aging time. The increase in hardness is never as great as in the rimmed steels, indicating a slower coagulation or a lesser amount of precipitated material. It will be noted that the intersections of the SMA curves with the zero line are consistently to the right of those for the rimmed steels, and that the SMA steel does not soften below the original (as quenched) hardness until the temperature of about 150 to 200 degrees Cent. (300-390 degrees Fahr.) is reached, while the rimmed steels soften to below the original hardness at as low temperatures as 75 degrees Cent. upon long aging. At low temperatures the SMA curve is below those for rimmed steels, and at higher temperatures it is above. Steel 20 has the same carbon content as SMA-15, and it is apparent that the difference in the behavior of the steels in the quench-aging test results from the differences in the deoxidation methods applied to these steels.

It may thus be said that though the irregular peaks observed in the curves point to the possibility of independent precipitation of oxides, the data are not sufficiently accurate and consistent to warrant any definite conclusions. It is apparent, however, that the precipitation hardening in the aluminum-treated steel is suppressed. As has been discussed earlier in this paper this suppression may be due either to the low oxygen content of these steels, to the retarding action of the finely dispersed alumina particles upon the diffusion of carbon in the ferrite, to the finer grain-size, or to the combined effect of two or all three of these factors.

#### SUMMARY

1. A series of steels was chosen representing a wide variation in the deoxidation practice and the carbon range of 0.02 to 0.25 per cent. These steels included rimmed steels, semi-killed steels, silicon-killed steels, and aluminum-killed steels.

2. Thirty-four steels representing the above four classes were tested for aging after quenching and for aging after cold working. Impact, hardness, and tensile tests were used for appraising the susceptibility of the steels to aging. The steels were normalized prior

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to aging tests; a few steels were also given aging treatments without previous normalizing, and three low oxygen steels, deoxidized with manganese, silicon, and aluminum, were tested for over-strain aging after they had been given a box-annealing treatment.

3. Deoxidation has a very pronounced effect on the over-strain and the quench-aging of mild steel. Generally, the more thorough the deoxidation the less marked is the tendency of steel to age.

4. Normalized rimmed steels are very highly susceptible to *quench-aging*, the maximum effect being reached in steels containing 0.04 to 0.05 per cent carbon. In the semi-killed steels the aging is considerably less than in the rimmed steels and the aging effect shows the same general tendency to diminish with increasing carbon content. The silicon-killed steels quench-age considerably, but only about half as much as the rimmed steels.

5. Steels killed with aluminum quench-age very little, the degree of aging decreasing with increasing carbon content. In the carbon range of from 0.2 to 0.25 per cent they become practically free from quench-aging.

6. Rimmed, semi-killed and silicon-killed steels are very susceptible to *over-strain aging* even in the higher carbon range. Aluminum-killed steels strain-age considerably less, the embrittling effect of the strain aging treatment decreasing with the degree of deoxidation.

7. In the "as-rolled" condition all steels are very susceptible to over-strain aging. However, the strain aged SMA steels possess a better impact resistance than the other aluminum-killed and semi-killed steels investigated.

8. The change in hardness with rising temperatures of quenching (300 to 715 degrees Cent.) was determined and correlated to the degree of aging after quenching. The degree of hardening of normalized steels upon quenching from subcritical temperatures decreases with increasing carbon content and with the degree of deoxidation, indicating that both carbon and oxygen are factors determining the degree of supersaturation of the ferrite and consequently the aging properties of steel.

9. In view of considerable variations in the grain-size with the method of deoxidation, a brief study was made of the influence of grain-size variations on the aging characteristics of steel. Fine grain-size resulting from deoxidation with aluminum is partly re-

sponsible for the comparative immunity of aluminum-killed steels to aging.

10. It is possible that highly dispersed alumina particles in the aluminum-treated steels may contribute to their non-aging properties possibly through decreasing the rate of carbon diffusion in ferrite.

11. The effect of time and temperature on the aging characteristics of several steels was studied by means of aging tests carried out at elevated temperatures (20 to 300 degrees Cent.). Using these data an attempt was made to demonstrate the independent precipitation of oxides.

12. Deoxidation decreases the tendency of mild steel to age, (1) because it lowers the dissolved oxygen content of the steel, (2) through the formation of finely divided particles of deoxidation products it refines the grain-size, and (3) possibly reduces the rate of carbon diffusion in ferrite.

## DISCUSSION

**Written Discussion:** By L. R. van Wert, Harvard Graduate School of Engineering, Cambridge, Mass.

One's comments on a paper of the excellence of this one must be largely confined to commendatory words. This paper is, as none can doubt, a signal contribution to the literature of aging. It would seem that one cannot now much doubt the cause-effect relationship between age-hardenability of steel (in either of its two manifestations) and the degree of its deoxidation. The statement (on page 624) ". . . . it will be noted that the hardening effect of cold-working alone is much greater in the rimmed than in the SMA steel," suggests this question: Is not the apparent greater work-hardenability of the steel of higher oxygen content simply a manifestation of the latter's greater age-hardenability, that is to say, is not much of the seemingly abnormal increase in hardness resulting from deformation of this steel merely the consequence of actual aging during the deforming operation?

**Written Discussion:** By John L. Burns, Republic Steel Corporation, Chicago.

This discussion refers only to aging after quenching from sub-critical temperatures.

The authors have set out to prove that deoxidation affects aging of mild steel and have concluded that the most effectively deoxidized steel is least prone to aging. The writer does not dispute the fact that deoxidation may affect the aging, but the authors have not proven their point.

In Fig. 7 the authors show the effect of carbon content on the points increase in hardness (Rockwell "B") due to aging for both rimmed and killed steels. In so doing they have apparently missed the meaning of their method of testing. The Rockwell "B" numbers are arbitrarily chosen figures to meas-

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ure hardness differences and so an increase of a given number of points over one portion of the scale has not the same meaning as a similar increase over a different range of that scale.

For example, a plot of Rockwell "B" hardness against tensile strength (or against per cent carbon in the annealed condition) results not in a straight line, but in a curve of the general form shown below.

Killed steels are harder than rimmed steels of similar carbon content and,

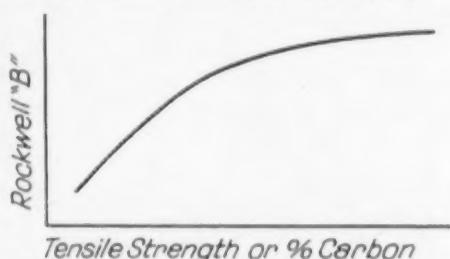


Fig. 1—Curve Showing General Form of Rockwell "B" Hardness and Tensile Strength.

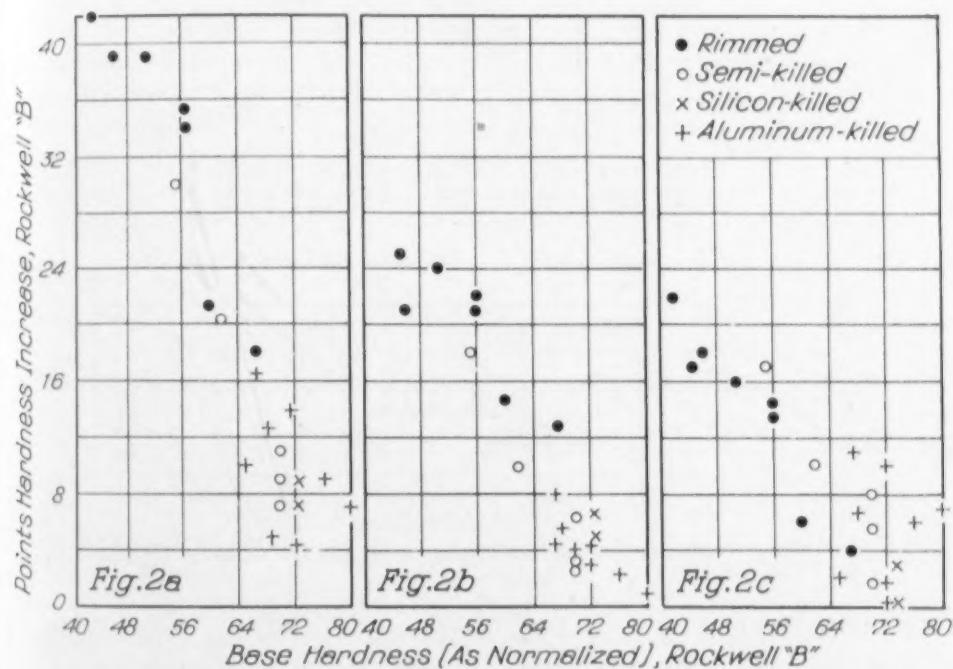


Fig. 2—Data Replotted from Table V for Rimmed, Semi-Killed, Silicon-Killed and Aluminum-Killed Steel.

therefore, the increase in hardness numbers will be less for killed than rimmed steels.

In Fig. 2 of this discussion the authors' results are replotted, where the points increase in hardness are plotted against the base hardness (as normalized hardness) instead of against per cent carbon. It will be noted that all of the types of steel are included in the hardness plot and that there is no

apparent difference in the points hardness increase for any type of deoxidation where the base hardness readings are similar.

The writer would refer the authors to his paper<sup>1</sup> which they have apparently overlooked, where the effect of increasing carbon content upon the aging

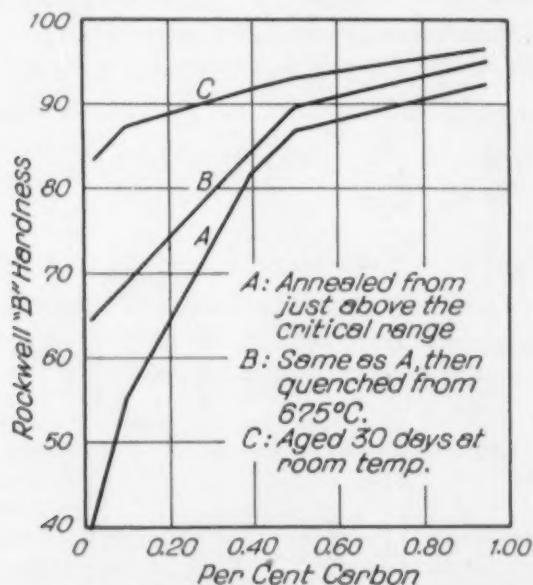


Fig. 3—Effect of Increasing Carbon Content on Hardness Changes Due to Aging of Plain Carbon Steels.

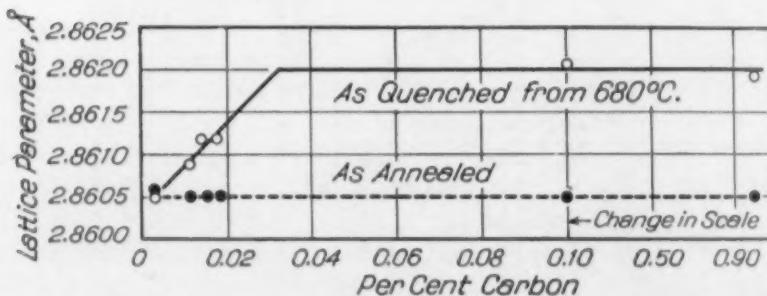


Fig. 4—Effect of Introduction of Carbon in Solution (Supersaturated) in Alpha Iron.

of steels is discussed. Fig. 3 of this discussion is reproduced from this paper and the following is quoted as an explanation.

"A plot in Fig. —— of the results in Table —— brings out the fact that the aging as measured by hardness increase in the higher carbon steels is very slight as compared to that in low carbon steels. This would tend to lend credence to the possibility that aging is due to oxygen, and that because oxygen in solution decreases with increasing carbon content the aging decreases. It should be pointed out, however, that changes in physical properties are not

<sup>1</sup>"Classification of Alpha Iron-Nitrogen and Alpha Iron-Carbon as Age-Hardening Alloys," John L. Burns, *Transactions, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1934.*

really a measure of precipitation, but an indicator. This is especially true when the original physical properties differ as they do in the case of low carbon and high carbon steel. The X-ray measurements bring this out quite clearly."

Fig. 4 of this discussion shows the X-ray results to which reference is made. The lattice parameter change for high carbon steels is the same as that for low carbon steels above 0.10 per cent carbon. The results for steels below 0.03 per cent carbon are for rimmed steels. The other steels are silicon-killed.

In summarizing, the writer contends that the authors have not proven that deoxidation affects the quench aging of mild steel but quite the contrary, i.e., that it is without effect.

#### Authors' Closure

The authors appreciate the kind comments of Dr. L. R. van Wert. Although no experimental confirmation was obtained during this investigation, the authors are inclined to share Dr. van Wert's opinion that much of the apparent increase in hardness resulting from the deformation of rimmed steel is merely a consequence of actual aging taking place during the deforming operation. To this it might be added that some of this apparent work-hardening is due to aging that has taken place immediately after the cold working operation, before testing. Certain time has necessarily been allowed to elapse between the deforming operation and the testing, and, therefore, considerable portion of the hardening here referred to as work hardening, must actually be due to aging in the first few seconds or minutes immediately after the deformation, when the rate of aging is the greatest.

The discussion by Mr. J. L. Burns gives the authors an opportunity to elaborate on certain points which have been treated elsewhere in the paper but apparently have escaped Mr. Burns' attention. In his attempt to show that the authors have not proved that deoxidation affects the quench-aging of mild steels, Mr. Burns steps into the slippery grounds of applying certain generalizations to a particular set of data obtained on a group of commercial steels.

Mr. Burns' graphs in his Fig. 2 showing the hardness increase upon aging, or quenching and aging versus the hardness of steels in the normalized condition, have no significance in the evaluation in the influence of deoxidation on the aging. The point of discussion in this paper is the increase of hardness of steel due to disintegration of solid solution (ferrite) obtained by quenching, i.e., aging. The amount of aging is determined by the amount of the precipitable solute in the ferrite of the quenched steel and the amount and degree of dispersion of the precipitated material upon aging treatment. These factors are by no means determined by the hardness of the steel in the normalized condition. Therefore there is no justification in basing any conclusions from graphs obtained by plotting the increase in hardness due to aging versus the hardness of normalized steels, and consequently, Mr. Burns' conclusions based on false premises are not correct.

In Fig. 1 of this closure the increase in hardness due to aging proper is

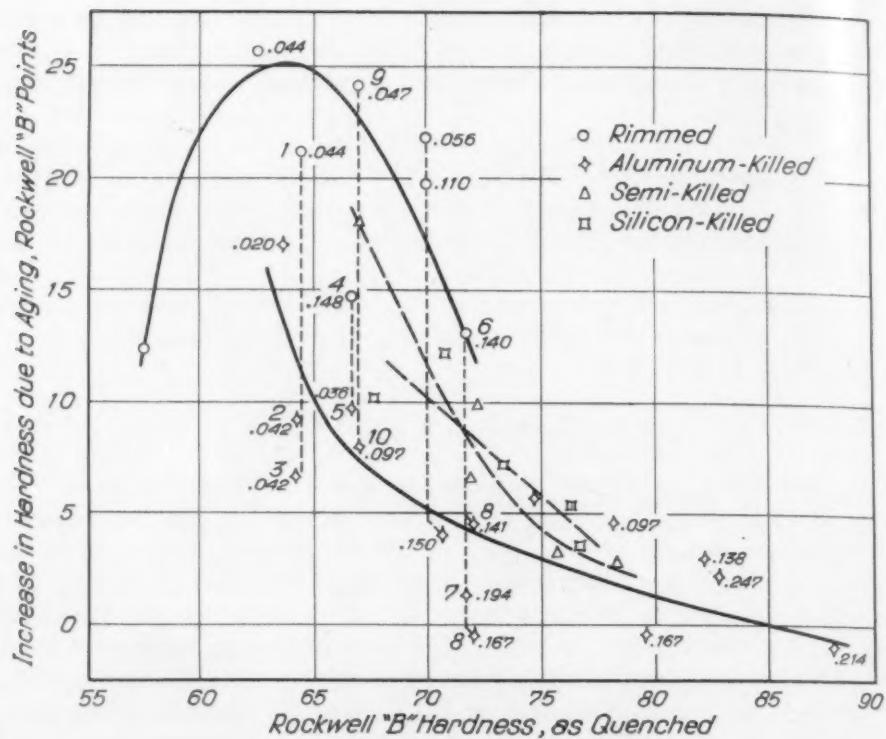


Fig. 1—Increase in Hardness Due to Aging Plotted Against "True Base Hardness."

plotted versus the "true base hardness," i.e., the hardness of steels in the as-quenched condition. It is true that in both types of steel (rimmed and killed) the amount of aging decreases as the "base hardness" increases, but the whole curve for the rimmed steels lies far above the curve for the killed steels. Comparison of points 1 with 2 and 3; 4 with 5; 6 with 7 and 8, and 9 with 10 indicates very clearly that the rimmed and the aluminum-killed steels of the same hardness in the as-quenched condition, or nearly the same carbon content, or both, behave quite differently, namely, the aluminum-killed steels in all cases age less than the rimmed steels.

In Fig. 2 of this reply the data of Table V are replotted to show the effect of carbon on the quench-aging. Quenched rimmed steels are represented by black dots, and quenched aluminum-killed steels by crosses. The values for the aged steels of both types are encircled. On the horizontal line  $A_1-A_3-A_5-A_7$  two rimmed and two aluminum-killed steels are picked out, of nearly the same initial hardness (as quenched from 700 degrees Cent.). Vertical lines drawn to points  $A_2$ ,  $A_4$ ,  $A_6$  and  $A_8$  representing the hardness of the same steels upon aging, indicate very clearly that the rimmed steels of the same initial hardness (as quenched) in all cases age more than the aluminum-killed steels. Points  $B_1$ ,  $B_3$ ,  $B_5$  and  $B_2$ ,  $B_4$ ,  $B_6$  serve further to illustrate this statement.

These data are sufficient to prove conclusively the fallacy of Mr. Burns' interpretation of the data presented in Table V. Sufficient data are given else-

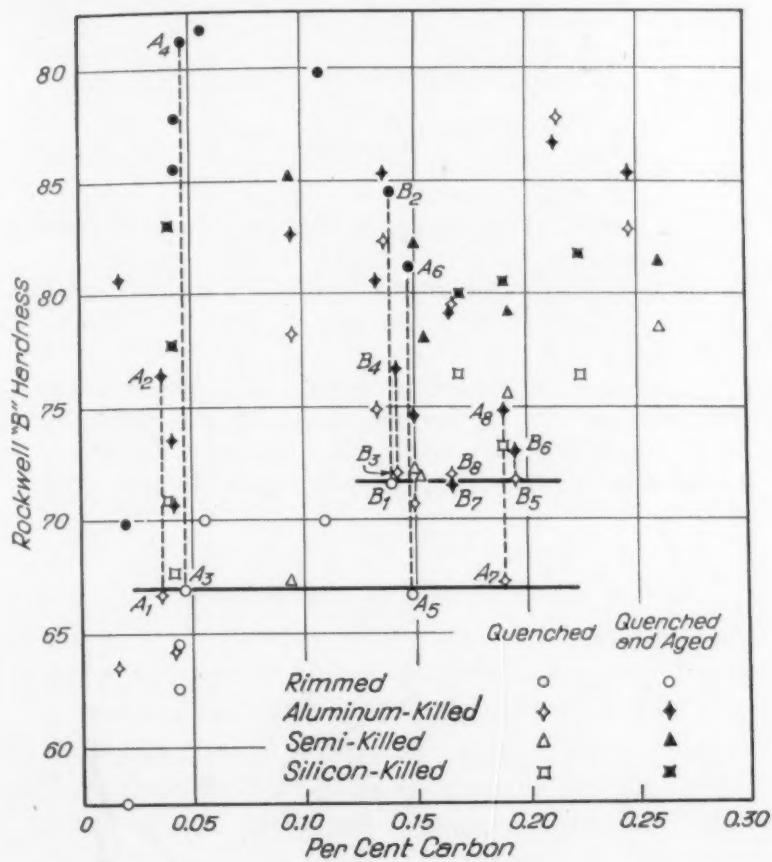


Fig. 2—Data of Table V Replotted to Show Effect of Carbon on the Quench-Aging.

where in the paper to show that although in both types of steel the aging is less the higher the carbon content and the higher the initial hardness, the aluminum-killed steels age consistently less than the rimmed steels of the same carbon content and the same initial hardness (in the as-quenched condition).

This conclusion is substantiated by other data given in the paper, and is in agreement with previous reports by other investigators, some of which have been mentioned in the first part of the paper.

## THE DIFFUSION OF ELEMENTS IN SOLID IRON

BY GERARD E. CLAUSSEN

### *Abstract*

*The nature of diffusion of elements in solid iron and steel is discussed from two standpoints:*

1. *Diffusion rates, a compilation of available data on which has been prepared;*
2. *Microstructure.*

*The changes in microstructure in steels and iron-copper alloys induced by isothermal addition and diffusion of phosphorus are closely related to, and may be partly accounted for by, ternary phase diagrams or chemical affinities.*

**D**IFFUSION, the movement of one material through another in the direction of a concentration gradient, is a fundamental term that is invoked in the elucidation of many physico-metallurgical phenomena, such as welding, aging, coreing, and banding. To be of assistance in explaining these phenomena in iron and steel, the term diffusion itself should be supported by quantitative data on diffusion rates and by acceptable notions of the mechanism of diffusion.

### DIFFUSION RATES

The quantitative measure of diffusion at a given temperature is the diffusion constant of the well-known Fick's Law. The information required to calculate the constant, usually denoted by  $D$  and expressed in  $\text{cm}^2/\text{day}$ , includes the time of the diffusion experiment and the concentrations of the diffusing element at the surface and at a known depth within the diffusion layer. The heat of diffusion,  $E$ , expressed in  $\text{cal/mol}$ , is loosely interpreted as the minimum energy that must be possessed by a diffusing atom in order to move about, and may be calculated from values of the diffusion constant at two or more temperatures. Values of  $D$  and  $E$  previously reported or calculated with the aid of layer analyses to which Fick's Law has not

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The author, Gerard E. Claussen, is research assistant, American Welding Society and Department of Mechanical Engineering, Polytechnic Institute, Brooklyn, N. Y. Manuscript received October 15, 1935.

Table I  
Diffusion Constants of Elements in Solid Iron\*

Element	Temperature Degrees Cent.	D cm <sup>2</sup> /day × 10 <sup>5</sup>	E cal/mol	Observer
Carbon (in CO)	800	130	30,000	(1)
	850	328		
	900	648		
	950	1020		
	1000	1730		
	1050	2420		
	1100	3880		
Nitrogen	550	185	31,000	(2)
	800	104		
	850	260		
	900	520		
	950	930		
	1000	1170		
	1050	2160		
Aluminum	900	33	49,000	(4)
	1000	170		
Silicon	960	65		(5)
	1150	125		
Tin	950	8.4	46,000	(6)
	1000	17.2		
	1050	34		
	1100	66		
Phosphorus	950	6.2	46,100	(7)
	1000	12.1		
	1040	21.6		
Oxygen	1000	6.5		(7)
Sulphur	950	2.6	26,700 (approximately)	(7)
	1000	4.8		
	1050	6.0		
	1100	8.6		
Molybdenum	1150	11.2	135,000	(9)
	1200	20-130		
	1200	5.9		
	1300	15-70		
Chromium	960	190-460		(10)
	1400	830.		
Manganese	1280	2.6		(5)
	1330	3.2		
Tungsten	1400	21-89		(11)
	1200	26		
	1200	0.8		
Nickel				(5)

\*The diffusion of a large number of elements in iron and steel has been studied, among others, by J. Laissus and by L. Guillet but their published results unfortunately cannot be used to calculate linear diffusion rates.

The rate of diffusion of hydrogen through iron has recently been determined by C. J. Smithells and C. E. Ransley (12).

hitherto been applied are collected in Table I. Needless to say, the experimental data are not of uniform reliability.

In view of the principal assumptions upon which Fick's Law is based, namely: that the material in which diffusion occurs remain isotropic and homogeneous, it is surprising that the majority of the elements diffuse strictly according to Fick's equation. A notable

exception is chromium at 1200 degrees Cent. (2190 degrees Fahr.) the diffusion constant for which is much lower in the more, than in the less, concentrated layers. Again, whereas Fick's Law may be strictly obeyed, the heat of diffusion may change with temperature, as in the case of sulphur. Among well over a score of proposed equations for expressing the diffusion of elements into metals, Fick's equation appears to be the most satisfactory and the least empirical.

The diffusion constant may also depend upon the manner in which the diffusing element is presented to the surface of the iron. The diffusion constant of carbon may be much higher from a fused cyanide bath than from an atmosphere of carbon monoxide at the same temperature; perhaps the liquid bath alters the surface potential and yields a higher carbon concentration at the surface.

The difference between the rates of diffusion of an element in alpha and in gamma iron is shown by the high value of D for nitrogen at 550 degrees Cent. (1020 degrees Fahr.). Although the qualitative nature of isothermal diffusion across a heterogeneous field of alpha and gamma has been described (6),<sup>1</sup> the quantitative course of the concentration-depth curve across such a field seems to require further study, for there may be an elbow in the curve (7), (8) at the compositions corresponding to the compositions of the conjugate alpha and gamma solid solutions, or there may be a discontinuity (10). The former course implies a difference in diffusion rate of the element in the two forms of iron, phosphorus thus appearing, according to Bramley's results, to have a higher diffusion rate in alpha than in gamma iron at 1000 degrees Cent. (1830 degrees Fahr.). The latter course suggests that the conjugate solid solutions have different compositions at the temperature of diffusion. The ideal isothermal concentration-depth curve across a heterogeneous phase field contains both a discontinuity and a change in diffusion rate corresponding to the conjugate solid solutions.

It is premature to draw general conclusions about the diffusion of elements in iron and steel from the meager results of Table I. Nevertheless it appears that the more rapidly diffusing elements are members of groups in the Periodic Table farther removed from Group VIII, the iron group, than the more slowly diffusing elements. The outer electron shells are therefore, as would be expected, important factors in diffusion. Other criteria of diffusion rate that

<sup>1</sup>The figures appearing in parentheses refer to the bibliography appended to this paper.

have been found useful in salts and nonferrous metals, such as crystal structure (13), cannot yet be developed for iron.

It is also difficult to explain the effect of impurities in the iron on subsequent carburization or nitriding. A small amount of sulphur in iron depresses the rate of diffusion of carbon far more than an equal atomic proportion of phosphorus or oxygen; the rate of diffusion of nitrogen in iron at 900 degrees Cent. (1650 degrees Fahr.) is actually increased by the presence in the iron of 2 per cent oxygen by weight. Fischbeck (14) has pointed out that the reduction in rate of nitriding at 550 degrees Cent. (1020 degrees Fahr.) by the presence of carbide in the steel is purely mechanical; the structural condition of the carbide, whether as grain envelopes or as spheroids, might then control the rate of diffusion to a great extent. That carbon and nitrogen diffuse at the same rate at 900 to 1100 degrees Cent. (1650 to 2010 degrees Fahr.) regardless of each other's presence may be due to the interstitial character of their austenite solid solutions.

#### MICROSCOPIC STUDY OF PHOSPHORUS DIFFUSION

The time-concentration characteristics expressed by diffusion rates are not sensitive indicators of the mechanism by which an element diffuses into iron and steel. Indeed, beyond the fact that activated adsorption of the diffusing element on iron is probably a necessary condition for volume diffusion, there is little that is definitely established about the atomic or sub-microscopic mechanism of metallic diffusion. The microscopic mechanism of diffusion of elements such as phosphorus in iron has, on the other hand, been explained and related to the binary phase diagrams (6), (7).

The microscopic mechanism of the diffusion of phosphorus into steel may be explained with the aid of the iron-iron carbide-iron phosphide diagram (15) of which two vertical sections derived from the results of R. Vogel are shown in Figs. 1 and 2.

Upon heating a 0.3 per cent carbon steel in phosphorus vapor at 930 degrees Cent. (1705 degrees Fahr.) phosphorus diffuses into austenite until, the phosphorus content reaching about 0.3 per cent according to Fig. 1, the surface of the specimen is converted to alpha phase containing phosphorus but very little carbon. As phosphorus continues to pass across the interface: alpha-gamma, the alpha layer is thickened at the expense of austenite which, at the junction with alpha, becomes richer in carbon. A layer of phosphide free from

carbon simultaneously forms on the outer surface of the columnar layer of alpha if the phosphorus pressure is adequate. When such a specimen is quenched from 930 degrees Cent. (1705 degrees Fahr.), the soft alpha case encloses a hard, high carbon core.

When a steel containing 1.3 per cent carbon is phosphorized at 930 degrees Cent. (1705 degrees Fahr.) no alpha layer is formed, in accordance with Fig. 2 in which no alpha field exists at 930 de-

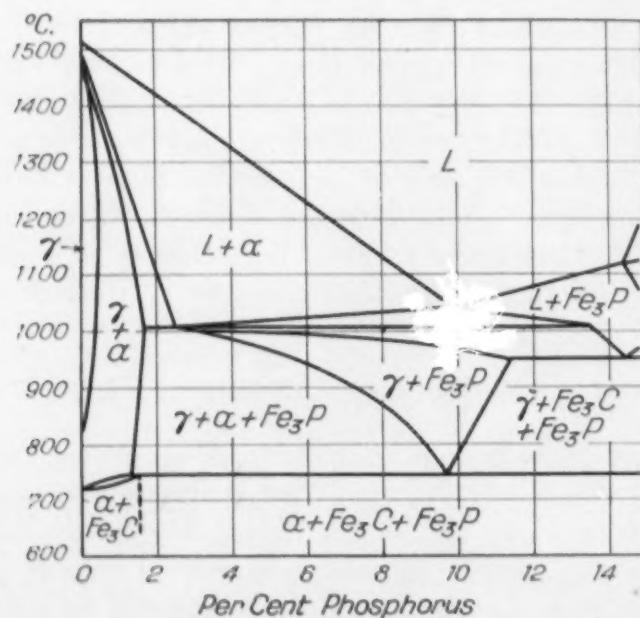


Fig. 1—Vertical Section Through Fe-Fe<sub>3</sub>C-Fe<sub>3</sub>P Phase Space Constant Ratio Fe:C—99.7 : 0.3 Derived from Diagrams by R. Vogel (15).

grees Cent. (1705 degrees Fahr.), but instead iron is abstracted from the austenite to form a carbon-free phosphide. The high carbon case on such a specimen water-quenched from 930 degrees Cent. (1750 degrees Fahr.) is shown in Fig. 3.

If phosphorization of the 1.3 per cent carbon steel is carried out at a temperature above 955 degrees Cent. (1750 degrees Fahr.), the temperature of the ternary eutectic: austenite-Fe<sub>3</sub>C-Fe<sub>3</sub>P, the product in equilibrium with austenite is no longer a solid, carbon-free phosphide but a liquid rich in phosphorus and carbon which "wets" the surface of the steel. In Fig. 4 this liquid, slightly hypoeutectic in agreement with Fig. 2, is shown penetrating along the grain boundaries of austenite.

Phosphorus-rich liquid also penetrates along the grain bound-

aries of the columnar alpha zone in 0.3 per cent carbon steel as shown in Fig. 5. A little Fe-C-P eutectic was added to the phosphide layer on this sample to reduce the melting point below quenching temperature, 960 degrees Cent. (1760 degrees Fahr.). Carburation of alpha by liquid is shown by the dark martensitic, partly fused border of the jagged band of alpha phase. Although the reaction between carbon-rich liquid and alpha has evidently been rapid, the diffusion of phosphorus has also been sufficiently rapid to maintain a zone of alpha separating the carbon-rich liquid on the outer

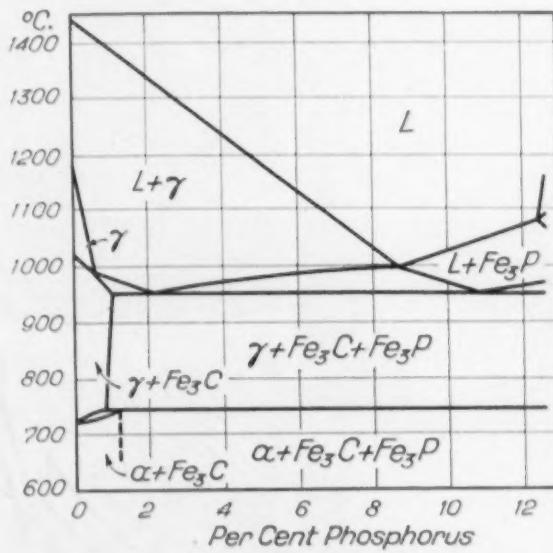


Fig. 2—Vertical Section Through Fe-Fe<sub>3</sub>C-Fe<sub>3</sub>P Phase Space Constant Ratio Fe:C—98.7 : 1.3 Derived from Diagrams by R. Vogel (15).

surface from the carbon-rich austenite on the inner. The gradual accumulation of carbon beneath the alpha zone during measurement of the diffusion rate of a loop-forming element into low carbon steel probably causes progressive reduction of the rate as the time of diffusion is increased.

The microscopic nature of phosphorus diffusion in iron-copper alloys at 950 degrees Cent. (1740 degrees Fahr.) is much the same as in low carbon steels; that is, a layer of columnar alpha crystals concentrates copper in the austenitic core. Although copper when pure is rapidly converted to phosphide in phosphorus vapor at temperatures as low as 600 degrees Cent. (1110 degrees Fahr.), it is extraordinarily resistant to phosphorization when it is alloyed with iron. The 50 per cent Cu-50 per cent Fe alloy shown in Fig. 6 was

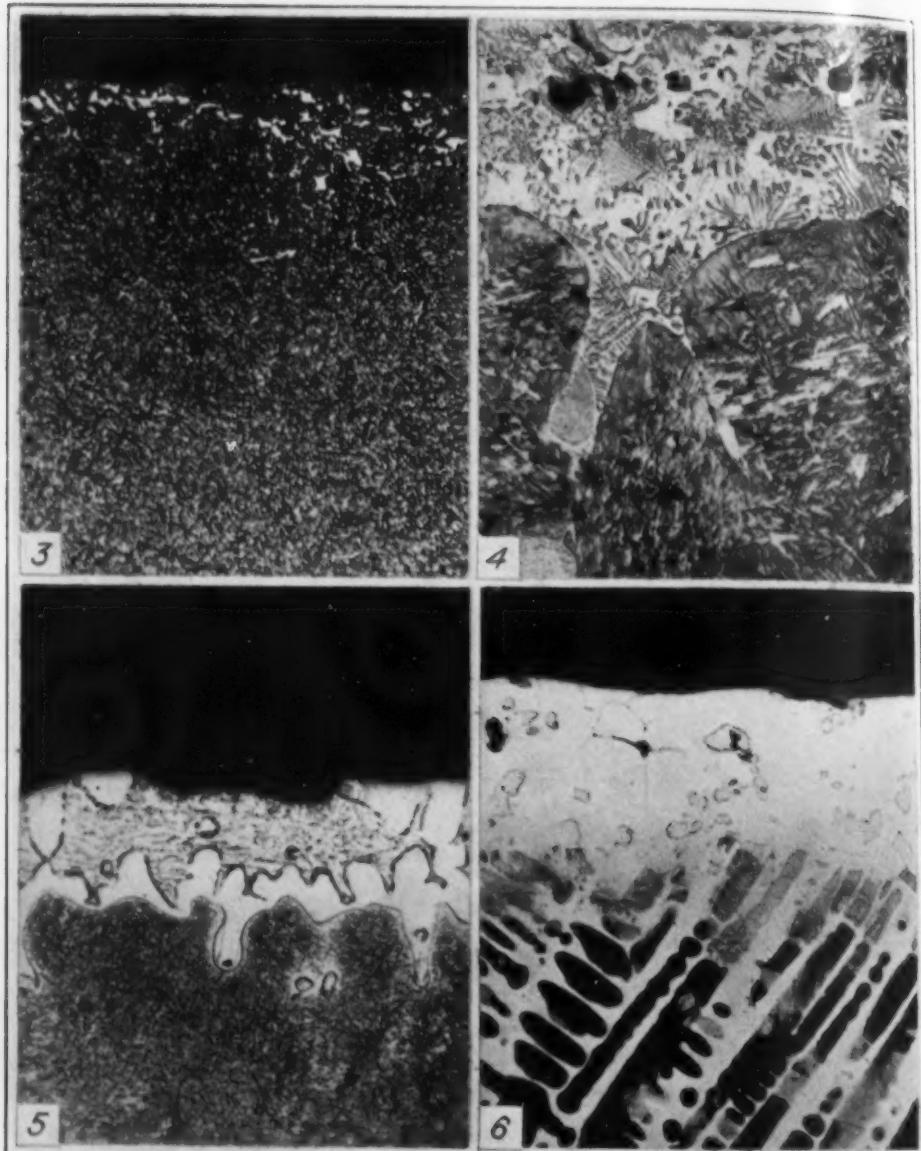


Fig. 3—Photomicrograph of 1.3 Per Cent Carbon Steel Phosphorized One Hour at 930 Degrees Cent. Water-Quenched. Etchant 5 Per Cent Nital.  $\times 100$ .  
 Fig. 4—Photomicrograph of 1.3 Per Cent Carbon Steel Phosphorized One Hour at 960 Degrees Cent. Water-Quenched. Etchant 5 Per Cent Nital.  $\times 500$ .  
 Fig. 5—Photomicrograph of 0.3 Per Cent Carbon Steel Phosphorized One Hour at 960 Degrees Cent. in Contact with High-Carbon Liquid. Water-Quenched. Etchant 5 Per Cent Nital.  $\times 100$ .

Fig. 6—Photomicrograph of 50 Per Cent Iron, 50 Per Cent Copper Alloy, Phosphorized One Hour at 1020 Degrees Cent. Slowly Cooled. Etchant 5 Per Cent Nital  $\times 100$ .

heated for one hour at 1020 degrees Cent. (1870 degrees Fahr.) in phosphorus vapor yet, aside from a thin network of copper phosphide at the extreme edge of the specimen, the copper was unat-

tacked. The iron, on the other hand, was converted to phosphide to a considerable depth below the surface. The stages in the conversion of iron to phosphide are illustrated in the photomicrograph. The austenite at 1020 degrees Cent. (1870 degrees Fahr.) is first converted to alpha, whose position is shown by the white band across the dendrites, then to a liquid of undetermined composition but of eutectic structure, and at last to massive iron phosphide. It may thus be concluded, by analogy with similar observations on the resistance to high temperature oxidation of copper in iron-copper alloys, that the heat of formation of copper phosphide is less than that of iron phosphide.

#### ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dr. W. R. Maddocks of the Faculty of Metallurgy, University of Sheffield, for encouragement and valuable suggestions.

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## OPEN-HEARTH TEMPERATURE CONTROL

By EARNSHAW COOK

### Abstract

*The calibration and use of optical pyrometers in steel making are discussed in detail. A workable system of temperature control for the open-hearth is suggested with reference to the limitations of instruments and melting practices. Operating data are presented together with such items of plant practice as may be benefited by successful application of the methods.*

ONE of the most important phases of steel plant practice involves the development and maintenance of uniform temperature control throughout the operations from blast furnace to finishing mills. Technical publications on this subject have been concerned largely with the calibration of optical and radiation pyrometers and include large amounts of valuable information as to the proper correction factors to be applied to temperature observations of molten and solid metals in the furnace under black body conditions where the object and its surrounding media may be at similar temperatures, or outside the furnace where they certainly are not. The most interesting dissertations have been published by the U. S. Bureau of Standards, by Adolph Fry<sup>1</sup> and Rudolph Hase.<sup>2</sup>

While the furnace man is little interested in the question of absolute temperatures if he is provided with a dependable method for obtaining comparable readings, certain suggestions translated from Fry's final summary may be repeated to advantage:

"On the basis of the observation that oxide or slag films on the melted metal as well as mirror-like streaks on streams of molten steel radiate practically like black bodies, it is recommended for the optical temperature measurement of fluid steel that use be made of the radiation of the brightest spots, oxide or slag films

<sup>1</sup>Adolph Fry, *Stahl und Eisen*, November, 1924.

<sup>2</sup>Rudolph Hase, *Archiv für das Eisenhüttenwesen*, Vol. 4, November, 1930.

A paper presented before the Seventeenth Annual Convention of the Society in Chicago, September 30 to October 4, 1935. The author, Earnshaw Cook, is research metallurgist, American Brake Shoe and Foundry Co., Chicago Heights, Illinois. Manuscript received February 15, 1935.

or mirror streaks, particularly since the present investigation has shown that the formerly customary measurements on the radiation from clear surfaces can lead to error. Since in technical practice optical temperature measurements are at present carried out in various ways and since there is no general agreement as to the absolute accuracy of the results obtained, it is urgently advised in the case of all such measurements that careful note be made of the particular method so that the values obtained will be comparable with other measurements."

Hase seems to have obtained similar confirmatory evidence in his investigation of the temperatures of cupola iron:

"Optical pyrometer measurements (of molten iron) showed the lowest apparent temperature at the taphole amounting to 2370 degrees Fahr. (1300 degrees Cent.) as compared to the thermo-couple indication of 2470 degrees Fahr. (1355 degrees Cent.). The curve shows that the further the measuring point moves away from the taphole the more nearly the apparent temperatures approach the true value which they reach with sufficient accuracy for all practical purposes at the end of the channel. This curve can well be interpreted in terms of progressive oxidation of the surface. If for this particular case, emissivity is calculated on the basis of the radiation formula, values are obtained which increase continuously from 0.62 at the taphole to 0.95 at the end of the channel."

Apparently the general dissatisfaction with temperature observation is not confined to American practice and may account for the reticence of investigators to include temperature measurements in published reports. Although reference is occasionally made to optimum tapping and pouring temperatures for killed or rimmed steels, the actual limits are frequently described as "neither too hot nor too cold." While technical comment and practice is calculated toward tapping temperatures so regulated as to produce 500 to 1000 pounds of ladle skull for top poured steel, the literature is comparatively restricted concerning practical methods of accurate temperature control for steel making.

#### CALIBRATION OF INSTRUMENTS

Temperature observations of molten metals have been more successfully attempted by the disappearing-filament type of optical py-

rometer whereby the glowing wire of a small electric lamp is blended against the light emitted by the particular hot body as received through a telescope provided with lenses and color screens suitable for the purpose. The lamp situated in the telescope is lighted and controlled from a portable case containing dry cells, variable rheostat and ammeter. Comparison is made of the current flowing through the blended filament as measured in milliamperes with that shown on a calibration chart previously standardized by similar observations of hot bodies at known temperatures over the range extending upward from 1100 degrees Fahr. (595 degrees Cent.).

In an effort to establish pouring temperature control in 1926 it was found impossible to check the readings of any two optical pyrometers in service against each other or as referred to the weight of ladle skulls from heats of similar chemical specifications. The variations from the calibrations occurred after the instruments had been in service for different and extended periods of time and appeared to result from any one of a number of conditions: unclean lenses, gradually deteriorating filaments, changing ammeter characteristics, et cetera. Such complete lack of confidence was so generally apparent in the observations that it became necessary to abandon the original calibrations and establish empirical standards which could be regularly and conveniently checked under operating conditions.

Fortunately this necessary reference point was provided by the apparent freezing of killed low carbon simple steel as simultaneously observed on the ingot tops with four different instruments over a series of heats briefly indicated in Table I.

Table I  
Ammeter Readings: Milliamperes

Instrument No.	Tapping Stream	Difference	Pouring Stream	Difference	Ingot Tops	Difference
1	456	0	424	0	430	0
2	462	6	432	8	436	6
3	468	12	440	16	444	14
4	480	24	452	28	454	24

It was at once evident that the average variations of freezing point readings in amperes were uniformly reflected throughout the normal working range and the observed datum point was arbitrarily designated "2760 degrees Fahr." (1515 degrees Cent.) as the mean temperature reported in the literature for the liquidus of 0.10 to 0.12 per cent carbon iron. Since graphs of the original calibration charts

against milliampere-temperature ordinates presented essentially parallel lines over the working range, the remainder of the temperature scale for the plant standardization was similarly determined by interpolation and, so used until December, 1927, permitted the establishment of a uniform system of temperature observation closely comparable within plus or minus 20 degrees Fahr.

The inauguration of open-hearth temperature control for an operation of seventeen 125-ton furnaces in the following year suggested a review of the calibration methods and, after considerable experimentation, it was found possible to obtain consistent readings of the melting points of  $\frac{1}{4}$ -inch copper, nickel, iron and platinum wires or strips fused in the open with direct current furnished by the motor generator set of the usual electric welding machine. The results of the original determinations are shown in Fig. 1 together with the makers' calibration of one of the instruments as received from the factory and corrected for emissivity.

The parallel agreement of the several instruments over the working range is apparent. The original M.A.-temperature curves of pyrometer No. 137162 gave the results shown in Table II.

Table II  
M.A.—Temperature Relationship of Pyrometer 137162

Element	M.A.	Melting Point Degrees	Black Body Calibration			Emissivity* Correction Degrees
			Fahr.	Degrees	Transition Pt.* Fahr. Degrees	
Platinum	499	3224	3060		3160	3355
Iron: C—0.10%	438	2760(?)	2660		2750	2905
Mn—0.15%						
Nickel	426	2650	2580		2660	2815
Copper	356	1980	1980		2040	....

\*Leeds and Northrup catalogue No. 86 from data compiled by U. S. Bureau of Standards.

It may be explained that the "black body" temperatures are those obtained from optical pyrometer observations within a uniformly heated furnace in which the temperature is measured by a standardized thermocouple; the "transition point" corrections are those for the reported difference between thermocouple temperatures and simultaneous observations in the open on liquid iron near the freezing point where an apparent change in the character of the surface occurs; while the "emissivity corrections" are those for the reported difference between optical pyrometer measurements of molten steel under black body conditions and in the open.

It should be thoroughly understood at this time that the purpose of the investigation was to establish a comparable, readily checked calibration of optical pyrometers for steel plant purposes, approaching absolute temperature values as a secondary consideration. Recognition of the reported laws of emissivity was included only insofar as the reference observations were made in the open with complete absence of black body conditions with the possibility that any necessary corrections might be thus automatically obtained.

One further concession was made in the final calibration; since the emissivity correction appears to be a linear function of the black

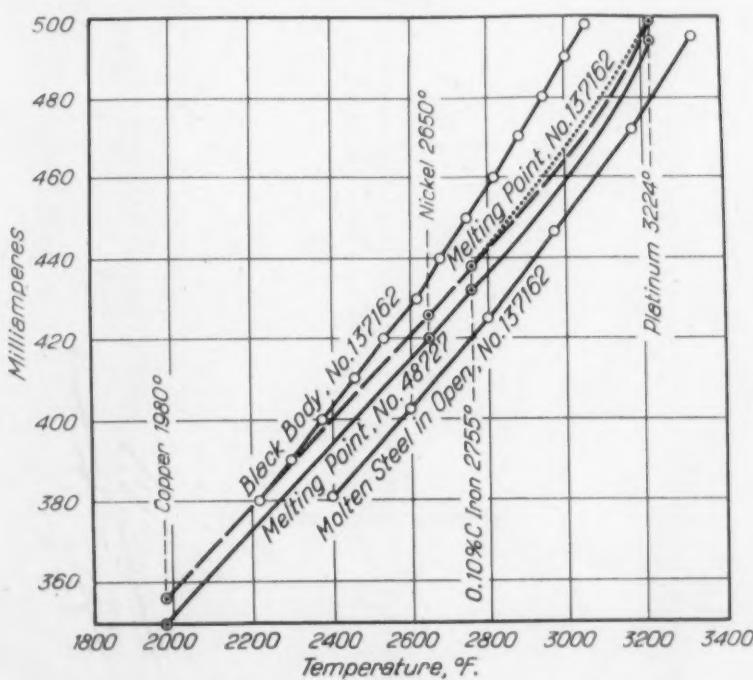


Fig 1—Direct Calibration Curves of Optical Pyrometers.

body temperature, it seemed more important that the best average straight line be drawn for the melting point calibration with black body versus emissivity correction ordinates (Fig. 2) than for those of milliamperes versus melting temperatures (Fig. 1). This in effect changes the melting point of 0.10 per cent carbon steel from 2760 to 2755 degrees Fahr. (1515 to 1512 degrees Cent.) and causes intersection of the black body calibration at 2250 degrees Fahr. (1230 degrees Cent.) just below the melting point of solid iron oxide which is reported to have an emissivity approaching unity. Iron oxide scale melts freely in soaking pit practice above 2250 degrees Fahr. (1230

degrees Cent.) where the emissivity is said to decrease<sup>3</sup> and continuously increasing positive corrections are required. It should be noted that the broken line for instrument No. 137162 in Fig. 1 should be used for M.A.-temperature calibrations with melting points as being more consistent with the corresponding emissivity corrections of Fig. 2 than the original curve.

Table III  
Tabulation of Emissivity Corrections for Steel in the Open  
(Reported within  $\pm 5$  Degrees Fahr.)

Black Body Degrees Fahr.	Melting Point Degrees Fahr.	Steel in Open Degrees Fahr.
2455	2500	2665
2470	2520	2685
2485	2540	2705
2500	2560	2725
2520	2580	2740
2535	2600	2760
2550	2620	2780
2570	2640	2800
2585	2660	2820
2600	2680	2835
2620	2700	2850
2635	2720	2870
2650	2740	2890
2670	2760	2910
2690	2780	2930
2705	2800	2950
2720	2820	2970
2735	2840	2990
2755	2860	3005
2770	2880	3025
2790	2900	3045
2805	2920	3065
2825	2940	3085
2840	2960	3105
2855	2980	3120
2870	3000	3140
2890	3020	3160
2905	3040	3180
2920	3060	3200
2940	3080	3215
2955	3100	3240
2970	3120	3255
2990	3140	3275
3005	3160	3295
3020	3180	3310
3040	3200	3330
3055	3220	3350

Graphs of the black body, transition point, steel in the open and melting point calibrations are shown in Fig. 2 and in tabular form in Table III. It would seem that the straight line relation of the black body and melting point curves in Fig. 2 might be more than coincidental. The relative accuracy of the latter would predicate closely corresponding emissivities in the liquid phase for the four metals employed in the experiments, which has been reported to be

<sup>3</sup>U. S. Bureau of Standards, Bulletin No. 91.

the case for platinum, iron and nickel.<sup>4</sup> To further examine this phenomenon, simultaneous temperature measurements were conducted with an optical pyrometer and a platinum couple in a special protection tube immersed in the hot top of a 0.10 per cent carbon killed ingot immediately after teeming. The thermocouple was pre-heated in the top of the previously poured ingot.

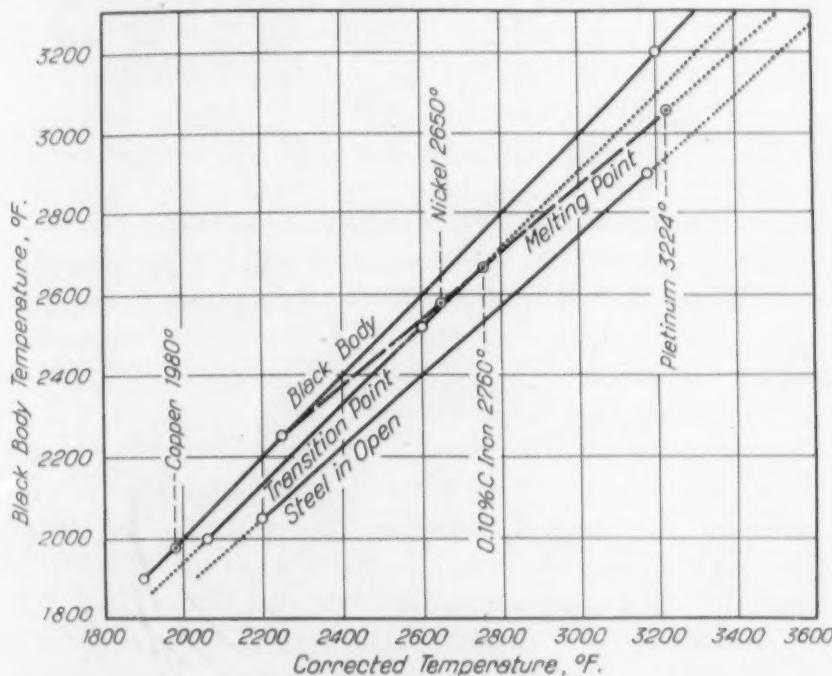


Fig. 2—Emissivity Corrections for Optical Pyrometers.

It is evident that the difficulties of calibration are complicated by uncertainties regarding the condition of the surface under observation. The thermocouple apparently failed to reach the freezing temperature at which the transition and melting point calibrations (columns 3 and 5) check. The correction for steel in the open (column 4) is obviously in error for the temperature of the solidifying surface. Is it then more reasonable to believe that supercooling and solidification phenomena may allow steel to be poured below the freezing point (Tables IV, VI, VII) or that the last metal poured in the hot top loses 140 degrees Fahr. (columns 3, 4) in temperature instantaneously? Is this an optical effect or an actual temperature increment resulting from the solidification of supercooled crystals of austenite?

<sup>4</sup>Communication, U. S. Bureau of Standards.

Table IV  
Simultaneous Readings of Optical Pyrometers and Platinum Couple

Pyrometer Observation	M.A.	Time of Immersion in Seconds		Thermocouple Temperatures Degrees Fahr.		
		(1)	(2) Black Body Degrees Fahr.	(3) Transition Point Degrees Fahr.	(4) Steel in Open Degrees Fahr.	(5) Melting Point Degrees Fahr.
Pouring Stream	436	25	2650	2735	2890	2740
Freezing Ingot Top	438	50	2660	2750	2910	2760
		70				2708
		85				

Since, however, the emissivity corrections are of more theoretical than practical interest if any accurately duplicable calibration is adopted, all specific temperatures hereinafter reported will be presented in both "melting point" and U. S. Bureau of Standards calibrations for "molten steel in the open" for purposes of general convenience and comparison. (Table III).

Further observation of freezing ingot tops based on melting wire calibrations indicated that these particular temperatures, constant for given chemical specification, decreased progressively from 2755 degrees Fahr. (1512 degrees Cent.) in direct proportion to the carbon content of the metal and averaged 2655 degrees Fahr. (1457 degrees Cent.) for 0.80 per cent carbon simple steel. These data are presented in Table V.

Table V  
Freezing Point Versus Carbon Content

Carbon M.A.	0.10 Per Cent	0.20 Per Cent	0.40 Per Cent	0.60 Per Cent	0.80 Per Cent
Black Body	2665° F.	2660° F.	2630° F.	2600° F.	2580° F.
Transition	2750° F.	2745° F.	2710° F.	2680° F.	2660° F.
Steel in Open	2905° F.	2900° F.	2865° F.	2835° F.	2815° F.
Melting Point	2755° F.	2750° F.	2715° F.	2680° F.	2655° F.

The readings are facilitated by breaking the solidified surface of the ingots with a rod when frozen to a depth of perhaps half an inch and prying up a sufficient section of the crusted steel to permit sighting the pyrometer upon the underlying metal. Thus protected, it will remain liquid for at least four minutes. The simulation of black body conditions has no effect upon the temperature readings. A very constant increment of 100 degrees Fahr. has more recently been ac-

curately observed<sup>8</sup> between the molten and solid phases under these circumstances. It would seem reasonable that the "transition" correction should correspond closely to this figure.

Plotting the freezing points of Table V with carbon-temperature ordinates definitely indicates correspondence with the iron-carbon liquidus. Further observation of the freezing points of killed steels poured in sand molds with a high speed recording radiation pyrometer having a lag of less than one second for full scale deflection shows a secondary and longer freezing point at a lower temperature, probably the solidus. It is not impossible that the metal may be poured in between the two as previously suggested. In general, it was learned that entirely comparable and dependable temperature observations might be obtained by regularly cleaning and checking the instruments, together with the strict ruling that no telescopes or control boxes be interchanged without recalibration. The care and

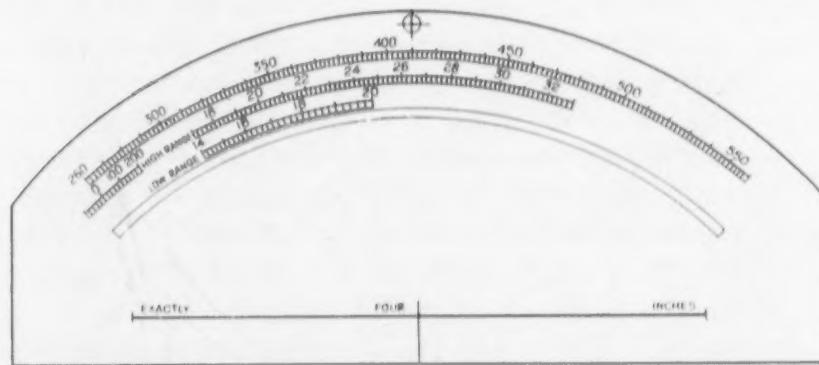


Fig. 3—Direct Reading Calibration Scale for Optical Pyrometers.

routine verification of the instruments is of paramount importance for temperature control: no pyrometer is satisfactory without meticulous attention to the details of operation and calibration.

A practical method for converting the standard Leeds and Northrup optical pyrometer to a direct reading instrument is illustrated in Fig. 3. A large scale drawing is made of the milliammeter dial as shown with datum points and a scaled four-inch reference line to check the accuracy of subsequent photostating. The desired temperature calibration is then inserted for high and low ranges with the melting temperature of 0.10 per cent carbon steel at 432 M.A. to allow for the maximum half-range variation of lamps and ammeters on either side. The direct reading scale is cut to fit the dial and the

<sup>8</sup>Communication, Messrs. Zweier and Hoey.

instrument standardized on any known temperature, in the open if it be preferred, with correct zero adjustment of the needle. If, for example, the pyrometer then reads 100 degrees too low, the telescope is disconnected and the zero adjustment is moved ahead a corresponding number of degrees. Since deflections are approximately uniform over the range no great error is introduced by this procedure. Standard 1.3 V, 0.5 A, S.C. base Thermo Guard Lamps without pins as manufactured by the Graybar Electric Company, possessing parallel electrical properties within the experimental error, may be confidently employed with this system of calibration.

#### PLANT METHODS

Accurate temperature measurement with optical or radiation pyrometers under usual operating conditions involves careful instruction of observers in the handling and care of instruments together with an intimate knowledge of their limitations. A consideration of special importance in developing temperature observation of molten steel appears at once: above the freezing point, temperatures consistent with operating practice seem best obtained by sighting the instruments to read the highest average temperature of the particular streams in general agreement with the findings of Adolph Fry<sup>1</sup> recommending that use be made of the radiation of the brightest spots rather than the clear surfaces of the molten metal.

If, however, this method of observation is attempted for pouring streams near the freezing point, there seems to be a decided tendency for reported teeming temperatures to approach those of the freezing points according to carbon content (2755 to 2655 degrees Fahr.) regardless of the amount of skull subsequently obtained in the ladle; in fact, with heavy skulls and sluggish streams it is difficult to obtain any reading other than the freezing point. It may be reasonable to suppose that the same phenomenon which obtains a constant temperature during the freezing of ingot tops is earlier induced in the colder, skulled heats and thus appears in the pouring streams. Nevertheless, when the observation of teeming temperatures is confined to the *darker* portions of the metal, ignoring the bright streaks as far as possible, the *readings* are generally *lower* than the freezing points, except for very hot heats, and are proportionately lower with increasing ladle skulls.

The "skulling point" as opposed to the "freezing point" has been

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considered as the lowest reported temperature at which uniformly heated steel may be poured with skulls limited to 1 per cent by weight of the melt—one to three thousand pounds according to the charge. It is interesting to note the existence of a constant difference of 80 to 85 degrees Fahr. between these several temperatures for killed steel based upon these calibrations. (Table VI)

Table VI

Carbon Content Per Cent	Freezing Point (M.P.)* Degrees Fahr.	Skulling Point (M.P.) Degrees Fahr.
0.05 to 0.15	2755	2680
0.35 to 0.45	2715	2635
0.75 to 0.85	2655	2575

\*These abbreviations will be used hereafter as follows for the various calibrations:

"B.B."—Black Body

"M.P."—Melting Point

"T.P."—Transition Point

"S.O."—Steel in Open.

While pure iron will certainly not solidify above 2790 degrees Fahr. (1530 degrees Cent.) nor remain liquid below that temperature under normal conditions, it is generally accepted that steel, as a solution of carbon, manganese and other metals with iron, possesses a progressive freezing range with the purer austenitic crystals separating out first. Although the difference in the observed temperatures of the so-called "freezing" and "skulling" points might be thus accounted for, the evidence may also be employed to support a theory of variable emissivity (or oxidation effect) for solid and liquid steels requiring a minimum positive correction of 80 to 100 degrees Fahr. on molten streams in the open-hearth temperature range.

Regardless of the theoretical background, a satisfactory and sensible system of temperature control has been developed by these methods of calibration and observation as will be presently set forth. With trained personnel and properly standardized instruments, the actual control of pouring temperatures within  $\pm$  20 degrees Fahr. and less than one per cent skull becomes comparatively simple as applied to the open-hearth practices. Schedules of desirable maximum teeming temperatures for top poured steel, allowing 40 degrees Fahr. above the skulling point, may be obtained from Table VII.

Specifically, the actual control consists in determining the average temperature drop per minute in the steel ladles from the start of full, continuous stream at tapping to the beginning of the pour as referred to the teeming temperature at the third ingot for

Table VII  
Pouring Temperature Schedule  
Killed Steel

Carbon Per Cent	Freezing Point* (M.P.) Degrees Fahr.	(S.O.)	Skulling Point (M.P.) Degrees Fahr.	(S.O.)	Maximum Pouring Temperature (M.P.) Degrees Fahr.	(S.O.) Degrees Fahr.
0.80	2655	2815	2575	2735	2615	2775
0.70	2670	2830	2590	2750	2630	2790
0.60	2685	2840	2605	2765	2645	2805
0.50	2700	2850	2620	2780	2660	2820
0.40	2715	2865	2635	2795	2675	2830
0.30	2725	2875	2650	2810	2690	2845
0.20	2740	2890	2665	2825	2705	2855
0.10	2755	2905	2680	2835	2720	2870
0.05	2765	2915	2690	2845	2730	2880
<b>Rimmed Steel</b>						
0.30	....	....	2650	2810	2690	2845
0.20	....	....	2665	2825	2705	2855
0.10	....	....	2700	2850	2740	2890
0.05	....	....	2720	2870	2760	2910

Because of an increased tendency for skulling, rimmed steel below 0.20 per cent carbon should be poured at slightly higher temperatures.

\*(Interpolated from 0.10 to 0.80 per cent carbon.)

heats of uniform bath temperatures. The readings are obtained by blending the filaments of the optical pyrometers for the highest average observation on the tapping stream with the ladle about one-half filled, and for the lowest average reading of the pouring stream. The time interval is measured to the opening of the stopper but the teeming temperature is observed during pouring of the third ingot as being more representative of the heat after the slightly chilled metal at the bottom of the ladle has been eliminated. A normal temperature loss of 20 to 40 degrees Fahr. occurs from the third to last ingots for 140-ton heats.

Other things being equal, the heat loss seems to vary principally with the time elapsed from start of tap to start of pour, excepting of course, the occasional vicissitudes of furnace practice. At the plant under investigation, killed steel lost temperature over this interval up to twenty minutes at approximately 10 to 11 degrees Fahr. average per minute; and up to thirty minutes, at approximately 6 to 8 degrees Fahr. average per minute. The greater portion of the actual temperature loss certainly occurs in the first five minutes: this is merely a satisfactory empirical method for regulating pouring temperatures. Average time-temperature-skull relationships are shown for a group of 150-ton heats in Tables VIII and IX. The "Temperature Range" column indicates the pouring temperatures at which the various heats were selected from the records.

**Table VIII**  
**Temperature Losses for 0.10 Per Cent Carbon Rimmed Steel**  
 (Note: All elapsed time reported in minutes)

No.	Heats	Pouring Temp. Range	Observed Temperature				Minutes Elapsed	Avg. Loss				
			M.P.	S.O.	M.P.	S.O.		Temp. Drop M.P.	per Min. M.P.	Avg. Skull Lbs.		
2775			2700	2940	2700	2850	12	9	21	240	11.4	2100
2790	9	2720	2955	3100	2720	2870	11	9	20	235	11.8	1200
2805	25	2720	2950	2995	2735	2885	10	9	19	215	11.4	1000
2820	32	2740	2960	3105	2755	2905	11	9	20	205	10.3	600
2830	27	2760	2960	3105	2775	2925	11	6	17	185	10.9	300
2845	25	2780	2965	3110	2810	2960	11	0	14	155	11.1	000
2855	25	2800										
2870												
2880												

**Table IX**  
**Temperature Losses for 0.80 Per Cent Carbon Killed Steel**

No.	Heats	Temp. Range	Observed Temperature				Minutes Elapsed	Avg. Loss			
			M.P.	S.O.	M.P.	S.O.		Temp. Drop M.P.	per Min. M.P.	Avg. Skull Lbs.	
10	2580	2780	2930	2575	2735	12	12	24	205	8.6	1500
10	2600	2800	2950	2600	2760	11	14	25	200	8.0	1200
10	2620	2800	2950	2615	2775	11	13	24	185	7.7	700
10	2640	2810	2960	2640	2800	12	12	24	170	7.1	500

It may be noted in Tables VIII and IX that the skull weights appear to be a function of both tapping and pouring temperatures. If similar heats of uniform but different bath temperatures are held to the same pouring temperature, the skull weights will correspond closely with each other and the holding period will, of course, increase progressively with the tapping temperatures. On the other hand, if the tapping and holding times are nearly identical (as occurs in most cases for Table VIII and IX) the pouring temperatures will increase proportionately with those at tapping.

The heats of the last item of Table VIII were scheduled for bottom pouring, were poured without delay and consequently exhibited considerably higher teeming temperatures (2810 degrees Fahr.) than several groups immediately above which were held for varying periods of time from similar tapping temperatures. The uniformity of many of the holding periods in Table IX (9 minutes) and Table VIII (12-14 minutes) resulted from an arbitrary and mistaken shop ruling that no low carbon heats be held longer than ten minutes and no high carbon heats, more than fifteen minutes. This order was subsequently rescinded with improved results when it was found impossible for the melters to regulate bath and pouring temperatures

within even these limits. This phase of the operation should be entirely a responsibility of the Metallurgical Department if accurate control is to be accomplished.

Because of irregular furnace practices, heats in the two lower temperature groups of Tables X and XI were not held in the ladle. While reported tapping and pouring temperatures are in general agreement with the weight of skull obtained, a definite increase in the average temperature loss per minute has been indicated.

**Table X**  
**Skull Weights Versus Pouring Temperatures—0.10 Per Cent Carbon Rimmed Steel**

No. Heats	Av. Wt. Skulls Lbs.	M.P.	Temperature			Pour Degrees Fahr.	Tap	Time Held	Total	Temp. Drop M.P.	Avg. Loss per Min. M.P.
			S.O.	M.P.	S.O.						
25	000	2965	3110	2765	2915	11	9	20	200	10.0	
25	1000	2950	3095	2725	2875	10	11	21	225	10.6	
25	2000	2940	3085	2720	2870	11	9	20	220	11.0	
25	3000	2930	3075	2720	2870	12	0	15	210	14.0	
25	5/8000	2920	3065	2700	2850	12	0	15	200	13.4	

It might be expected that the observations of badly skinned heats should disclose lower tapping temperatures rather than increased temperature losses per unit of time, as would be the case if it were possible to obtain the exactly correct average tapping temperatures. This situation appears to be the result of nonuniform temperature gradients from the top to the bottom of the bath. Because of small initial

**Table XI**  
**Skull Weights Versus Pouring Temperatures—0.80 Per Cent Carbon Killed Steel**

No. Heats	Av. Wt. Skulls Lbs.	M.P.	Temperature			Pour Degrees Fahr.	Tap	Time Held	Total	Temp. Drop M.P.	Avg. Loss per Min. M.P.
			S.O.	M.P.	S.O.						
10	000	2810	2960	2660	2820	10	15	25	150	6.0	
10	1000	2800	2950	2640	2800	12	12	24	160	6.7	
10	2000	2790	2940	2600	2760	12	13	25	190	7.6	
10	3000	2760	2910	2595	2755	16	0	21	165	7.9	
10	4000	2750	2900	2590	2750	15	0	18	160	8.9	

metal flow, fumes and ladle additions, it is not usually possible or practical to report continuous temperature observations from the start of tap until the slag appears. It has been found, however, that several confirmatory observations with the ladle one-third to one-half full furnish sufficiently representative temperatures to establish the desired and workable control.

As tabulated on page 664, careful instruction of observers in the mutations of open-hearth practice indirectly responsible for irregular bath temperature gradients is essential to successful temperature control. After due reflection upon furnace practice and tapping temperature, the nicety of judgment exhibited by experienced observers and melters in not delaying heats of questionable uniformity is evident. The constant heat losses for regularly used ladles, as well as the approach toward constant temperature with liberation of the heat of fusion at the skulling point may be expected to decrease the temperature drop per minute as the interval from tap to pour is increased. Thus, while the methods are by no means infallible, a thorough understanding of optical pyrometry as applied to steel making will permit the establishment of an open-hearth temperature control of surprising regularity and effectiveness.

The experience with 140-ton heats reveals that excessive skulling

Table XII  
Minimum Tapping Temperature

Carbon Per Cent	M.P. Degrees Fahr.	S.O. Degrees Fahr.
0.80	2760	2910
0.70	2775	2925
0.60	2790	2940
0.50	2805	2955
0.40	2820	2970
0.30	2835	2985
0.20	2850	3000
0.10	2865	3010

results from holding heats in the ladle tapped at or below the temperatures listed for the various grades of steel in Table XII. Such melts should be teemed at once without delay even before completely draining the furnace: clean pouring is more important in these instances than ultimate furnace yield.

Given average heat losses and time studies for a particular shop, the procedure for holding steel to temperature in the ladle is shown in the following tabulation:

Ordered Carbon .....	0.10 Per Cent	0.80 Per Cent
Tapping Temperature (M.P.) .....	2930 Degrees Fahr.	2830 Degrees Fahr.
Time Tapping .....	12 Minutes	10 Minutes
Estimated Average Loss per Minute .....	11 Degrees Fahr.	8 Degrees Fahr.
Scheduled Pouring Temperature (M.P.) .....	2700 Degrees Fahr.	2600 Degrees Fahr.
Total Necessary Loss .....	230 Degrees	230 Degrees
Total Time Required .....	22 Minutes	29 Minutes
Time of Hold: End of Tap to Open- ing of Stopper .....	10 Minutes	19 Minutes

Temperature control being subject to certain important limitations, its success consequently depends upon uniform furnace practice and the skill of melters and observers. Attempts to control tapping temperatures in the furnace for regulation of teeming temperatures are abortive and, because of unavoidable irregularities of the time cycle during tapping, can lead only to excessive skulls or extremely hot pouring. The only safe method apparently lies in tapping the steel at temperatures uniformly high enough to allow for usual tapping or operating delays and holding the heats for a calculated interval in the ladle. Estimation of the required bath temperature for any grade of steel may be made as follows:

Specified Carbon .....	0.10 Per Cent
Average Length of Tap .....	12 Minutes
Time Allowance for Long Tap .....	6 Minutes
Time Required to Move Ladle over Molds .....	3 Minutes
Total Safe Time Limit .....	21 Minutes
Average Temperature Loss per Minute .....	11 Degrees
Average Total Temperature Loss (11°x21") .....	230 Degrees
Scheduled Pouring Temperature (M.P.) .....	2700 Degrees Fahr.
Safe Minimum Tapping Temperature (M.P.) .....	2930 Degrees Fahr.

Normally the pouring of every melt of steel may be delayed for temperature control without risk, but the holding of heats under any of the listed circumstances making for nonuniform bath temperatures is hazardous to both skulling and pouring practice:

1. With more than 60 to 65 per cent cold charge except for very careful furnace practice.
2. With basic iron below 0.85 per cent silicon.
3. With too rapidly worked heats, or excessive stone charges.
4. With heavy lime or bottom boils at or near tapping.
5. With fuel shut off the furnace for more than five minutes immediately before tapping.
6. After reactions in furnace or ladle at tapping.
7. With long, slow tapping, or cold heats.
8. With cold ladle additions exceeding 0.75 per cent by weight of the heat.
9. For heats of seriously delayed charging.
10. For furnaces approaching the end of the campaigns.
11. And finally it is dangerous to hold heats more than twenty minutes after the end of the tap, particularly with more than six inches of slag covering the steel. The subsequent cutting action of the slag too frequently results in burned off rods.
12. It should also be noted that temperature losses per unit of time vary considerably from shop to shop and, while similar to those reported, are not necessarily identical or even nearly enough so as to permit exact duplication of practices.

While the difficulties involved in open-hearth temperature control appear formidable, intelligent co-operation between blast furnace, open-hearth and metallurgical departments can readily obtain 80 per cent of the heats tapped and poured within scheduled limits. The advantages of such practice may be found in a general trend toward: improved uniformity of bath temperatures, fewer badly skinned heats and increased ingot yields; less erosion of nozzles and better pouring practice; increased mold life and elimination of "sticker" ingots; fewer ingot and corner cracks; improved rimming for open steel; and decreased pipe losses and segregation for killed steel.

#### SUMMARY AND CONCLUSIONS

1. Sufficiently accurate temperatures of molten steel may be obtained with optical pyrometers carefully standardized upon known, constant temperature points.
2. While the actual temperatures reported are not important if they remain closely comparable, an approximate calibration may be obtained by reference to the known melting points of pure metals as observed in the open.
3. The accepted emissivity corrections for the apparent temperatures of molten steel might well be the subject of further investigation.
4. The freezing points of killed steel ingots offer a convenient means for checking the standardization of optical pyrometers under service conditions.
5. Observation of the highest average tapping temperature, during the stage when the ladle is approximately half full, and the lowest readable pouring temperature at the third ingot, permits the development of a generally consistent system for open-hearth temperature control.
6. Safe minimum tapping and pouring temperatures may be established for each grade of steel according to particular shop practices.
7. The control of pouring temperatures may be accomplished by holding heats in the ladle for a predetermined interval calculated from the initial temperature, length of tap, average temperature loss and the scheduled teeming temperature.
8. Certain limitations of temperature control imposed by variable furnace practices have been suggested.

9. A practicable schedule of freezing, skulling and pouring temperatures has been presented based upon the reported system of calibration and observation.
10. Possible operating advantages accruing to uniform temperature control in the open-hearth have been suggested.

#### ACKNOWLEDGMENT

The most sincere appreciation is extended to Messrs. R. D. Zweier, Willis Wirt, William Roberts, respectively, Chief Observer, General Pit Foreman and General Mold Yard Foreman, Maryland Plant, Bethlehem Steel Company, and Carl W. Potter, Chief Observer, Steelton Plant, Bethlehem Steel Company, and their organizations, with all of whom it was both a privilege and a pleasure to work during their accomplishment of effective temperature control in the open-hearth.

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#### DISCUSSION

**Written Discussion:** By M. J. Bradley, Leeds and Northrup Company, Philadelphia.

We are much interested in Mr. Cook's paper on open-hearth control and we wish to compliment him for his contribution in this important field. There undoubtedly is more divergency of opinion concerning the temperatures of open-hearth baths, tapping and teeming than in any other phase of steel production. Not only is there disagreement as to the actual temperatures involved, but also in the methods and means of measuring them. Let me mention, if you please, some methods now employed in different shops for measuring open-hearth bath temperatures. In some shops the melter estimates the temperature of the bath by the appearance of the end of a low carbon rod which has been melted off in the bath. This may or may not be supplemented by pouring a small amount of metal from a sampling spoon and noting its solidification. In another shop the same temperatures are measured by inducing a rod or ore boil which causes the metal to float up through the slag and the temperature of the metal is measured by an observer with an optical pyrometer. In some shops the flame is turned off during the measurement, in others it is left on. In other shops optical readings are made through an air protected pipe extending through the slag into the bath. In other shops various types of immersion couples are being tried out. Tapping temperatures are also measured in many different ways. The optical method, as present, predominates; however, here again considerable disagreement exists on what temperatures to measure and where to measure them. In the majority of shops the measurements are made on the darker areas of the tapping stream; others measure the lighter patches, and some take the reading from below on the metal stream close to the end of the spout.

The various methods and means employed to measure temperatures in

the open-hearth process, combined with the uncertainties entailed in emissivity corrections for various conditions and the possibilities of superheating or supercooling, explains in a great measure the discrepancies encountered in relating reported temperatures for similar heats in different shops. As Mr. Cook points out, it is very desirable, especially from an operating standpoint, to be able to reproduce accurately a temperature relation for the same step in the process in similar heats. It is desirable also to be able to transmit temperature information from one shop to another in such a way that it will have the same meaning to all parties concerned. To do this it is important that the instruments be accurately calibrated against a common standard; the reading must be taken in the same way under the same conditions; and, if corrections to take care of non-black body conditions are applied the magnitude of these corrections should be definitely stated. It would be desirable also to be able to use the same calibration to measure temperatures of the steel during processing as well as in the molten condition.

It is recognized generally that any instrument which is subjected to the rough usage an optical pyrometer sometimes receives in an open-hearth shop must be checked from time to time against suitable standards and the necessary adjustments or corrections made. The method most generally employed for doing this is to have a checking instrument maintained in the laboratory as a secondary standard. Instruments used in plant routine are then checked periodically against the standard instrument using a flat filament lamp or a suitable small furnace as a source of temperature. The ammeters may be independently checked against a standard potentiometer. If such a procedure is adopted generally the calibrations of one laboratory should agree with the calibrations of other laboratories. An "arbitrarily designated standard, such as the apparent freezing of killed low carbon simple steel" might possibly result in a handicap in shops which seldom make low carbon steel but specialize on high carbon and alloy heats.

The method of making the temperature readings should not present serious difficulties. It would appear that a standardized method could be worked out which would be acceptable to the industry.

The question of the corrections to be added to the apparent temperatures taken under definite sets of conditions, other than under "black body" presents a different problem. We are not satisfied that this problem can be eliminated satisfactorily by adopting an arbitrary standard in the open. We agree with the author that "the accepted emissivity corrections for the apparent temperatures of molten steel might well be the subject of further investigation."

Mr. Cook has introduced a subject which is exceedingly important in the open-hearth industry. We feel that it is sufficiently important that we take the liberty of suggesting to this Society that they consider appointing a committee to study the methods and means of measuring temperatures in the steel industry, with the idea of developing standardized procedures and results.

**Written Discussion:** By Gordon B. Wilkes, professor of heat engineering, Massachusetts Institute of Technology, Cambridge, Mass.

The author has certainly made a real advance in the practical technique of making a very difficult temperature measurement and this paper should lead to an improvement in open-hearth temperature control.

The calibration of an optical pyrometer by sighting on  $\frac{1}{4}$ -inch copper, nickel, iron and platinum wires or strips in the open introduces, in my opinion, some uncertainty on account of the variation of the emissivity of the different surfaces between themselves as well as with the rate of heating and outside light effects. A very well known means of checking an optical pyrometer against change of calibration is one using a variable lamp illuminating a ground glass and a standard pyrometer for comparison. This method should be more accurate than observing melting points in the open and checks can be made in a very few minutes.

Until there is more information concerning the emissivity of the surfaces involved in open-hearth temperature measurements, the true temperature as measured with an optical pyrometer will be uncertain but the author's investigation has undoubtedly reduced this uncertainty considerably and has given some very useful pointers toward the more precise control of open-hearth temperatures.

**Written Discussion:** By H. P. Munger and J. W. Poynter, metallurgical department, American Rolling Mill Co., Middletown, Ohio.

The author is to be congratulated on his investigation of tapping and pouring temperatures, of which a knowledge is necessary to improve the quality of the steel. It seems unfortunate, however, that almost all theoretical considerations are disregarded in his calibration of the optical pyrometers. In any calibration of optical pyrometers two points must be carefully considered, namely, that the temperature of the radiating source is constant and known, and that essentially black body conditions exist. When calibrating an optical pyrometer against the surface of a solidifying ingot none of these conditions are fulfilled. As pointed out by the author, a solidifying ingot "possesses a progressive freezing range with the purer austenitic crystals separating out first" and this causes the calibration point to be very uncertain, since a 0.1 per cent carbon steel has a rather wide solidifying range. Moreover, it is probable that the surface of the molten metal will become coated with oxide, which may be at a lower temperature, causing the results to be questionable. Under the conditions of the calibration, black body conditions would not exist unless the pyrometer was sighted in the crevice at the interface of the molten metal and ingot mold. It is possible that temperature measurements using this method of calibration could be duplicated where a standard procedure is used at a single plant but it seems improbable that comparison of results between different plants using this method of calibration would be satisfactory.

If the black body temperatures for the melting points of iron and nickel in Table II are corrected for the emissivity of the solid oxide of the metals, they agree more closely with the known melting points of these metals than when they are corrected for the emissivity of molten iron and steel in the open (See Table II "Emissivity Corrections"). The results would probably agree even better if care is used to shield the metal strips from stray light radiation.

There are several convenient methods for the checking and the calibration of optical pyrometers. One of the most convenient of these methods is to sight the pyrometer on a calibrated tungsten strip lamp under black body conditions. With a known current flowing, the tungsten strip emits a con-

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stant intensity of radiation and forms an excellent and reproducible source for calibration work. If an optical pyrometer calibrated by the National Bureau of Standards is used only for calibrating and checking, the tungsten strip lamp may be used as a transfer standard and need not be calibrated. With the current constant, the temperature of the tungsten strip is read first by the calibrated pyrometer and then by the one being calibrated.

If neither of these arrangements is considered satisfactory, a reproducible source of radiation may be obtained by inserting a thermocouple through the bottom of a crucible and placing it in the uniformly heated zone of an electric tube furnace. If the uniformly heated zone is rather long, substantially black body conditions exist and it will be rather difficult, if not impossible, to see the tip of the thermocouple. Sighting the telescope into the tube furnishes a simple means of periodically checking the constancy of the pyrometers. A duplicate check may be obtained by reading the temperature of the thermocouple tip using a telescope calibrated by the National Bureau of Standards and reserved for calibration and checking work only. This method may also be used for calibrating optical pyrometers, since the radiating source, at a given temperature as measured by the thermocouple, is always reproducible.

After an optical pyrometer has been satisfactorily standardized, the results obtained with it in controlling the open-hearth teeming practice can be compared with a high degree of certainty with the results obtained at other plants. If the true temperatures are desired, the usual "iron and steel in the open" correction can be applied, but for purposes of comparison of readings taken under the same conditions, no correction need be applied. It does seem very important in carrying on such work to have a method of calibration which is not subject to variations of the surrounding conditions, and which has a constant reproducible source of radiation.

**Written Discussion:** By C. N. Treat, Republic Steel Corporation, South Chicago.

The comparison of data in individual shops and particularly from different shops on tapping, teeming and skulling temperatures has always presented a problem because of various methods of calibrating or the lack thereof.

Mr. Cook has suggested a method which appears very practical in its application and we believe that any recommendations along these lines should be welcomed and tried by all of us who realize the importance of temperature control in the production of quality steel.

Mr. Cook mentions and undoubtedly emphasis should be placed on the absolute necessity of co-operation between the production men, superintendents, melters and foremen, with the technical men, metallurgists and observers. There must be a definite agreement as to the results desired, importance of these results and the methods to be used to obtain them. We feel that this is the first and most important step in control of any kind.

In the plant methods of applying temperature control, although we agree with the author generally, there are a few points which we believe can be discussed profitably.

The first is the reading of teeming temperatures. It has been our experience that the reading of the coldest part of the stream leads to confusion and very often erroneous results due to fumes and irregular streams and we obtain

more consistent and comparable results by reading the brightest part of the stream. No attempt is made to predict the amount of skull from the teeming temperature as we believe that with few exceptions quality steel, particularly forging grades, should be teemed well above the skulling point.

The second point is in regard to the rate of temperature drop in degrees per minute. This is very interesting and we would like to ask Mr. Cook how much variation is found in heats of similar analyses and identical tapping temperatures. It is quite possible, that, although the averages fall in line nicely, the results obtained by strict adherence to this plan might cause some trouble unless all conditions are met on the greater majority of heats.

The differences in shop practices can be shown by the fact that we agree quite well with the author on skulling points but generally are 10 to 15 degrees lower. Also, we find only a 10 to 15-degree drop during the teeming of a heat with often a slight increase on the last few molds teemed. This however, indicates to us that after the first short period, approximately 10 minutes, the temperature drop is comparatively slow.

In regard to the twelve conditions listed in the latter part of the article it is logical to assume that the amount of cold charge, the per cent of stone charged, and delay in charging, and analysis of the iron, are questions of furnace practice and slag control and should be entirely taken care of before the heat is ready to tap.

If by "too rapidly worked heats" the author means addition of cold iron, spiegel, or iron ore shortly before tapping there can be no question but, outside of this, the rapidity with which any heat can be worked depends upon the sharpness of the furnace and the operator.

The presence of furnace reactions or boils, ladle reactions and slow taps are obviously danger signs in temperature control and usually predict poor quality as well.

The danger of cold ladle additions should be qualified to except those which are strongly exothermic in reaction.

The likelihood of non-uniform temperatures being found in heats tapped during the end of a furnace campaign depends on the shop practice, furnace sharpness, etc., but the author should perhaps include in his list the fact that the first few heats tapped after a shutdown are almost invariably nonuniform heats.

These exceptions may seem trivial but if temperature control is to be effective it must be extended to cover as many heats as possible and in order to do this a thorough understanding of the various questions must be had.

**Written Discussion:** By Robert B. Sosman, Research Laboratory, United States Steel Corp., Kearny, N. J.

I believe it was Dr. Whitney who remarked, many years ago, that it is the instinct of the scientist to look at all sides of a question and see all the difficulties, all the reasons why a proposal will not work, while the practical inventor or the inventive technical man concentrates on the reasons why it ought to work and ignores all the difficulties that he is not absolutely forced to recognize. Knowing that every radiating surface has its characteristic emissivity, and that its brightness, and hence its apparent temperature, depend on that emissivity, a physicist can hardly be expected to endorse a method of

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pyrometer calibration which completely ignores the existence of such a property as emissivity. He assumes offhand that it cannot possibly work. In refutation, this paper contains the evidence that Mr. Cook has successfully controlled the pouring temperature of steel without concerning himself overmuch with that troublesome property.

Perhaps the meaning of the new data contained in the paper will be clarified if I am permitted to assume the role of the high-brow physicist and to relate some of the data.

Table IIA, below, contains the data of the author's Table II, interpreted as determinations of the emissivity of certain metals melted in wire or strip form by an electric current in the open air. This is a perfectly straightforward calculation from a set of physical measurements, involving no empirical calibrations and no assumptions except that we possess independent knowledge of the melting temperatures.

Table IIA

Metal	Cook's Brightness temperature	Known melting-point	Deduced emissivity
Platinum	3060°F	3224	0.61
Iron (C = 0.10%) (Mn = 0.15%)	2660	2760	0.68
Nickel	2580	2651	0.74
Copper	1980	1981	1.00

In every case the emissivities are considerably higher than those generally accepted as characteristic of the solid and liquid metals. For copper, nickel, and iron the reason obviously is that we are not observing the clean metal, but a mixture of metal and oxide, or an oxygen-saturated metal, or even a pure liquid oxide. Which of these it is might be determined by making corresponding observations in a vacuum or in a reducing gas. Why the emissivity for platinum should be high is not clear; the generally accepted is less than 0.4 for both solid and liquid. But whatever the surfaces are whose emissivity is being measured, the group of four makes a series in which the emissivity progressively decreases with rising temperature and the relation is not far from a straight line. That is probably the reason for the straightness of the author's calibration curve, which permits the system to be successfully used.

As a practical result, the author has shown pretty clearly that by completely disregarding emissivities and not worrying about them, he can reproduce a method and a set of figures that will control the pouring of the usual varieties of carbon steels. Unless we want true temperatures with which to make comparisons from one plant to another, or with which to study the chemistry of the process, nothing else need be asked for.

On page 653 the author refers to the apparent straightness of the emissivity correction as a function of the brightness temperature ("black body temperature"). It is not, of course, quite a straight line, but has the curvature represented by the formula:

$$\frac{1}{T} - \frac{1}{T_b} = \frac{\lambda \ln E}{C_2}$$

in which  $T$  = absolute temperature in  $^{\circ}\text{K}$  = Centigrade temperature + 273.1  
 $T_b$  = absolute brightness temperature = degrees Cent. as read by the optical pyrometer + 273.1

$\lambda$  = wave length of monochromatic light used in optical pyrometer =  $0.653 \times 10^{-4}$  cm

$C_2$  = Planck's second constant of radiation = 1.432 cm = degrees Cent.  
 $\ln E$  = natural logarithm of emissivity of surface

Fig. 1 shows the correction to the brightness temperature in its relation to true temperature, for a surface of emissivity 0.40, which is the value recommended by the Bureau of Standards for clean steel in the open. It is evidently a curve which does not depart greatly from a straight line. The fact that the departure is small, I think, accounts for the fact that the author obtains by his second series of calibrations a straight line.

Incidentally, the upper curve in Fig. 1 is of some interest, as a convenient

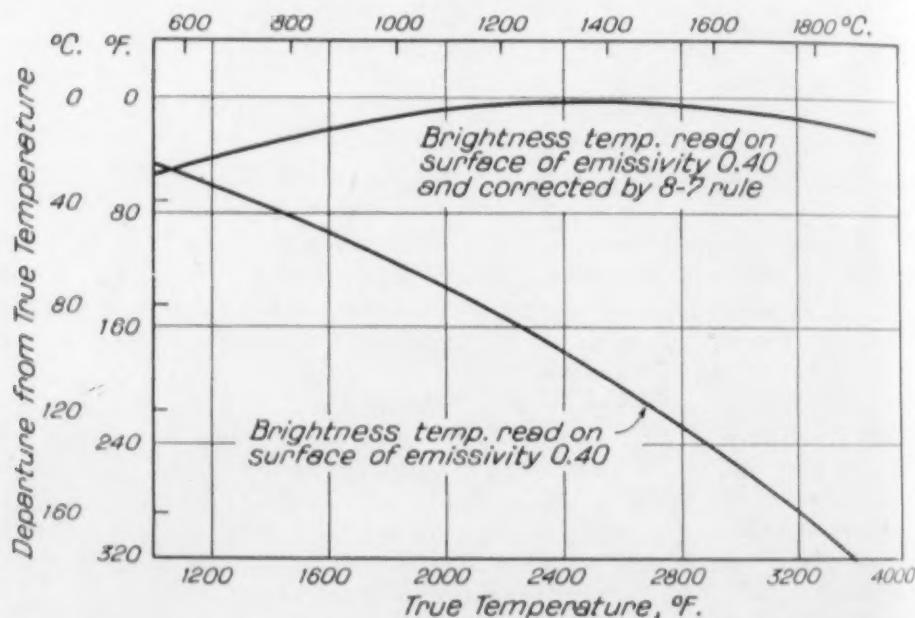


Fig. 1—Correction to the Brightness Temperature in Its Relation to True Temperature.

short-cut for correcting for an emissivity of 0.40. I call it the "eight-seven rule." Multiply the brightness temperature in degrees Fahr. by eight, take off 1000, and divide by seven, and the result between 2300 and 2700 degrees Fahr. is within a very few degrees of the true temperature as corrected for emissivity 0.40, without the inconvenience of carrying a set of tables in your pocket. The derivation of the rule is obvious from Fig. 1, in that a tangent to the lower curve in the vicinity of 2500 degrees Fahr. crosses the axis of zero correction at 1000 and has a slope of  $\frac{5}{6}$ .

The subject of the cause and rate of the cooling of steel in the ladle has always interested us. Fig. 2 shows the loss of heat in a ladle as calculated for 100 tons of steel tapped at 1600 degrees Cent. at 11½ tons per minute, into a ladle with a 7½ inch fireclay brick lining, and poured between fifteen and forty minutes after the beginning of the tap. The end of the tap and the beginning of pouring are indicated by the markers on the base-line of the figure.

The drop in the temperature due to radiation from the stream while the steel is running out is a constant. After the steel gets into the ladle it continues to radiate from the stirred surface until enough slag has gathered to cover the surface and practically insulate it. The uncertain and variable part of the heat loss is not the radiation loss, but the diffusion of heat into the refractories. That is where most of the heat goes, even when the ladle is mildly preheated. At the beginning, when the first few drops strike, they are practically chilled. Then comes the rapid rise in temperature as the ladle fills, and at about the end of the tap the steel is at its maximum out-of-furnace temperature. Then follows the effect of the continued diffusion of heat into the refractories and the steady drop, theoretically increasing in rate as the amount of steel that can supply heat to walls and bottom is diminished.

The loss from the top of the slag by convection of air is almost nothing. The loss from the outside of the ladle is not measurable.

It is evident from Fig. 2 that it is incorrect to assume a constant rate of

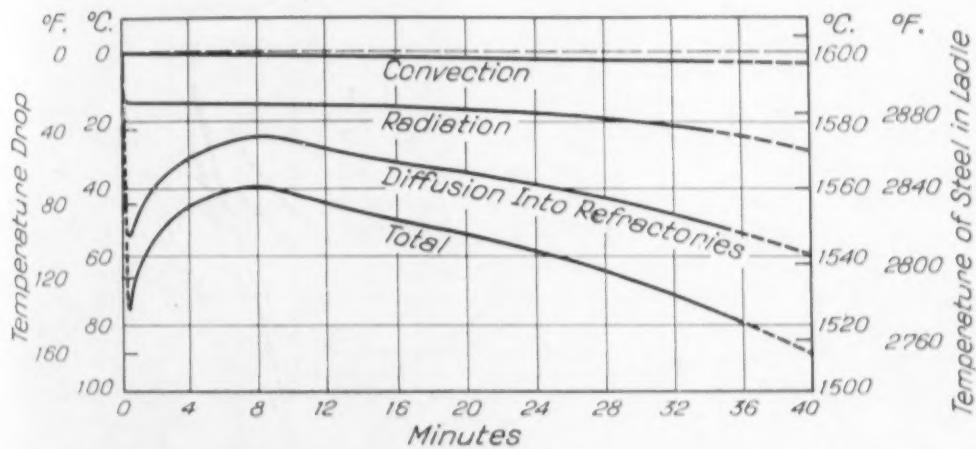


Fig. 2—Calculated Maximum Drop in Temperature for 100 Tons of Steel Tapped at 1600 Degrees Cent. at 11.75 Tons per Minute into Ladle with 7.5 Inch Firebrick Lining; Poured Between 15 and 40 Minutes from Beginning of Tap.

fall from the tapping temperature, whether the time be taken from the beginning or end of the tap. The rate is, however, approximately constant after the maximum has been passed. If an initial drop be assumed, effective at any definite time such as the beginning or the end of the tap, the cooling rate can then be safely taken as constant. In the case described in Fig. 2, this initial drop, assumed at beginning of tap, is about 30 degrees Cent. (55 degrees Fahr.). It tends to be automatically provided in the record when a method of reading such as the author's is used, which incompletely corrects for the low emissivity of the liquid metal when the temperature is measured on the tapping stream.

Another important consideration is the character of surface on which optical readings are made. The correction for an emissivity of 0.40 applies only to the smooth, clean liquid surface, appearing dark by contrast with the brighter portions, which are produced by channels in the surface or by oxidized films. The difference between these two kinds of surface cannot be accurately defined, but our experience indicates that it is of the order of 30 degrees Cent. The author's temperatures on the tapping stream were from the "highest average observation" (p. 660), and hence were evidently on the brighter surfaces; his corrections for emissivity, as represented by the columns headed "S. O." are therefore too high. On the pouring stream, however, where the "lowest average reading" was taken, the corrections applied are justifiable. It follows that the true drop in temperature between tapping and pouring is not as great

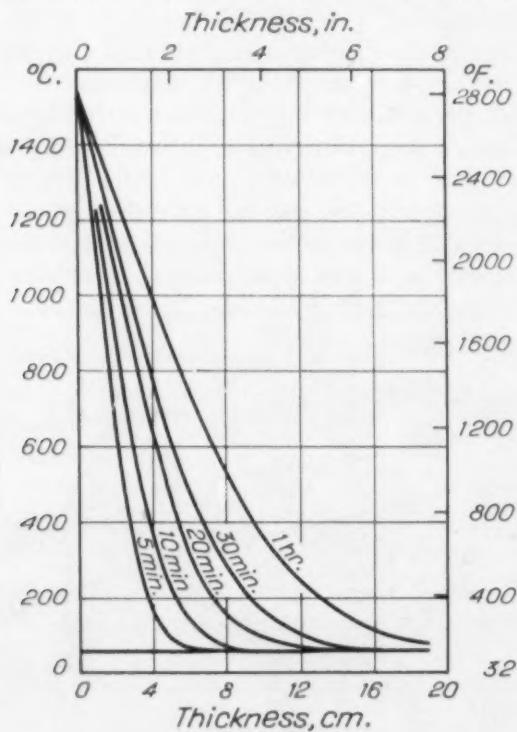


Fig. 3—Distribution of Temperature in the 7.5 Inch Firebrick Lining of a Ladle Containing Steel at an Intitial Temperature of 1585 Degrees Cent.

as shown in the author's tables, being nearer 175 degrees Fahr. than the 200-220 degrees Fahr. shown. The former figure is still appreciably larger than the estimate represented in Fig. 2, though the agreement is not bad when the numerous variables are considered.

Fig. 3 gives the set of curves upon which the estimates of heat absorption in Fig. 2 are based. It shows the change of temperature in the fireclay brick lining when a ladle 100 inches inside diameter and 113 inches deep is assumed to be level full of steel at an initial temperature of 1585 degrees Cent. The calculations are not exact, but are sufficient to show the form and interrelation

which applies only to the brighter oxidized films. At 60 degrees Cent. the highest average surfaces; 1 "S. O." is the "lowest". It follows that as great

of the temperature curves. The method using Gauss' probability integral was employed, and the basic data are: initial temperature 60 degrees Cent.; heat capacity 0.225; thermal conductivity 3.75 milli-calorie per sq. cm per sec. per degree Cent. per cm; bulk density 2.0 gram per cc.

Up to ten or twenty minutes after tapping the temperature rise at the outside of seven and one-half inches of fireclay brick is hardly detectable. Hence the insulation of a seven and one-half inch lining would have no appreciable effect on the heat loss unless the ladle were strongly preheated.

### Oral Discussion

DR. C. H. HERTY, JR.:<sup>1</sup> The method used at the Carnegie Steel Co. is notable. The temperature of the bath is obtained before deoxidation by inserting a rod in the furnace and causing a boil on the rod so that the metal shows over the slag, and an optical pyrometer is sighted on this boil, the gas being shut off on the furnace. This was checked a number of times and it was reported that the temperatures taken in the furnace indicated that you could obtain as reliable temperature in the furnace as you could at the spout if you took this boil test properly. It is reported that it took two or three months to train observers so that their measurements could be considered really accurate. The observation of a temperature before deoxidation is extremely important in judging how much deoxidizer is to be added to the bath.

W. J. REAGAN:<sup>2</sup> I would like to compliment Mr. Cook on his very fine job on the calibration and use of optical pyrometers. An investigation of this type of work is certainly needed. However, I believe that Mr. Cook has painted too pretty a picture of the value of the optical pyrometer. In our work we have not found the optical pyrometer values as reliable as he has indicated, particularly on readings of the molten metal as it is being tapped from the furnace. Gases and smoke obscuring the vision of the observer make these readings very unreliable. Another thing that should be very carefully pointed out is that the figures presented are only of value in the plant in which they have been obtained. We cannot compare values obtained in our plant on high carbon steel, with figures obtained in some other plant, with the same type of instrument and on the same kind of steel. There seems to be no comparison at all, just what causes the readings to be so unreliable is hard to figure out.

In taking optical pyrometer readings we have found that one of the most important things to be considered is that the operation should be standardized. By this I mean that the readings should be taken at the same time in each heat, and at the same point in the stream of metal, and by as few observers as possible. We have had similar experiences as Mr. Cook in taking readings at different points in the stream and we like to take them at the hottest point. These points usually appear at some place where the stream becomes straggly. When a stream is smooth and not broken up we do not get as high readings. Just why we obtain higher readings when the stream is not smooth is not at all clear, however, the readings obtained on the straggly stream seem to indi-

<sup>1</sup>Research Engineer, Bethlehem Steel Co., Bethlehem, Pa.

<sup>2</sup>Edgewater Steel Co., Pittsburgh.

cate more correct temperature values than readings obtained on the smooth stream.

Dr. Herty mentioned a method of taking temperature readings that originated at Homestead. A cold rod is inserted through the wicket hole into the bath of metal, the resulting boil causing enough metal to be uncovered to allow a temperature reading to be taken with an optical pyrometer. It takes a skilled observer to obtain readings by this method but readings seem very reliable.

While actual values (correct temperatures) are always of interest, the practical open-hearth man is principally interested in obtaining comparative values, that is relative values that may be consistently obtained. The difficulty with the optical pyrometer is that such values cannot be obtained. Variation in calibration and obscuring of the vision of the observer by smoke and fumes that often are so slight as to go unobserved but still making considerable variation in the temperature readings obtained, are the usual difficulties.

We have tried to obtain the freezing points of steel by sighting on the top of an ingot as it solidifies, but such readings are not satisfactory. I believe that Mr. Munger also pointed out the difficulty of obtaining readings in this manner.

As correct temperature readings are a very vital problem to the open-hearth operator, this paper gives us great stimulation to continue our efforts to obtain correct temperature readings in the open-hearth practice.

C. E. SIMS:<sup>8</sup> Mr. Cook gives an imposing array of figures which should be of undoubted value to a person making the grade of steel mentioned. I do not wish to discuss the figures given, but I do want to mention some precautions found necessary, based on a good deal of experience taking temperatures of casting steel. In the first place, there seems to be a considerable difference of opinion as to just how the temperature should be taken with an optical pyrometer. The bright and dark streaks in the streams of steel cause the greatest confusion. The writer settled this matter to his own satisfaction several years ago while making a large number of observations. These bright streaks in the streams will vary a great deal in their apparent temperature, variations of over 100 degrees being very common. The readings taken on the darkest portion of the stream are more consistent. Two men using different instruments and taking simultaneous readings can easily agree within a 10-degree range. That has been done repeatedly in our shop. My explanation for this is that the darkest portion of the stream gives the only correct reading. The darkest portion will always be found to be a smooth, convex surface. The bright streaks are concave surfaces where we have not only emitted light, but also reflected light. Small side streams also give reflected light. With a very smooth stream coming from the nozzle, correct readings will result, but with a ragged stream, bright streaks are present which always give high readings.

Mr. Cook also discussed the rate of temperature drop. Taking temperatures at the spout we have found to be very unsatisfactory on the whole. Usually

<sup>8</sup>American Steel Foundries, Research Laboratory, Indiana Harbor, East Chicago, Indiana.

the stream is too ragged and it is too difficult to get a clear sight on a smooth portion of the stream to obtain an accurate reading. The best that can be done is to take an average result from several readings, and consider it a bit higher than the true temperature. Making this allowance, we have found that the temperature drop from the spout during tapping to the earliest reading that may be obtained in the steel teemed from the nozzle will differ from 150 to 200 degrees. Practically all readings that we have taken have been in this range of difference. I attribute this rapid drop to the heat absorbed by the ladle lining itself. There is some loss due to the passage of steel through the air and to ladle additions of cold alloy, but I think the drop is principally due to the heat absorbed by the ladle itself. From the time of the first opening of the nozzle, to the last opening of the nozzle, there is an unimportant drop in temperature. In pouring castings we have noted occasionally that in pouring many small castings there will be a progressive drop for a while, and then when a large casting is poured and a prolonged heavy stream of metal is emitted, the temperature will rise again. Apparently, in short pours most of the metal comes from the bottom of the ladle or close to the walls. This metal is cooler. When a rapid stream of metal is poured, it comes down from the center where it is hotter.

E. B. BUNTE:<sup>4</sup> Some time ago I had the opportunity of looking over some heat records of five different steel companies, and noted the variation of tapping and pouring temperatures. There seemed to be five different standards with which the optical pyrometers had been calibrated. Each steel company seemed to have a different calibration (standard) from the others.

I think this body should take up the offer given to us by Leeds and Northrup for experimental work on the basis of making a standard method for the calibration of steel temperatures. The Bethlehem Steel Co. will be perfectly willing to go along with any experimental work in the hope of having a uniform calibration on temperature throughout the industry. We are perfectly willing to do any experimental work in our plants, or in any one else's plant. We are in hopes of having a standard calibration for the steel industry.

#### Author's Reply

These various discussions of the suggested method of open-hearth temperature control have been most interesting and instructive. We would like to leave one particular impression with you, however. The system of open-hearth temperature control described is a method, but certainly not the only method as has been brought out in the discussion. The question raised by Mr. Munger as to the duplication of the calibration can best be answered by saying that the calibrations of the instruments have been sufficiently standardized on the freezing points at various carbon contents from 0.05 to 0.85 per cent. In five shops with twelve, five, seven, eighteen and twenty furnaces respectively, the calibrations set up in the several plants can be checked within plus or minus 20 degrees with instruments that are transported from one to another. However, that is only one method for doing the job: so long as the methods are standardized under specific conditions of calibration and

<sup>4</sup>Bethlehem Steel Co., Bethlehem, Pa.

observation, nothing else is necessary. The lack of standardization of instruments has been the greatest factor in preventing open-hearth temperature control. This is because instruments with deflection type ammeters will not and do not stay on calibration for great periods of time, especially if they are used frequently. They may often go off calibration between heats and for that reason we prefer using a method which the observer can check directly on the job to one which requires instruments to be sent to the laboratory for calibration. While we realize that the calibration of the instruments is important, we are a little bit sorry that more of the discussion did not refer to actual open-hearth practice. Any calibration is workable although we think it would be highly desirable if, by conference and interchange of results, a generally acceptable method of calibration and observation could be standardized for the various temperature control problems throughout the country. We would like to thank Mr. Treat for his discussion of plant practices with which we are in general agreement. In one item suggested by Mr. Treat, we think it important to correlate pouring temperatures with skull. If the skull can be limited to a satisfactory minimum we feel that better results may be obtained for quality.

We agree with Mr. Sims in preferring observation at the darkest portion of the stream. This has been emphasized more on the pouring streams because there we seem to get less dependable results. It has been said that our tapping observations were made of the highest average temperature near the end of the spout. At that portion of the stream it will be agreed that the general appearance is dark rather than white: the bright region appears as the furnace stream becomes more ragged farther away from the spout.

Reports of the temperatures of molten steel have invariably been criticized for not explaining clearly the methods of calibration and observation employed. The paper has attempted to avoid this mistake by showing four parallel methods of calibration in Figs. 1 and 2 and in Table III. Careful reading will bring this out without confusion.

In the section devoted to plant methods only two calibrations are presented for each series of readings; that recommended by the Bureau of Standards and that employed in this investigation. This was intended to make the observations directly comparable with those of plants using the Bureau corrections. It would probably simplify the entire proceeding if temperature readings were reported in milliamperes as is understood to be the practice at one mill!

None of the methods of calibration is satisfactory: the empirical data behind them is a fertile field for investigation. The open-hearth superintendent is less concerned with precise temperature readings than with comparable observation and control. This is available within the limitations of men and instruments. We have attempted to criticize the latter constructively.

## PREFERRED ORIENTATION AND ROLLING CHARACTERISTICS OF LOW CARBON STRIP STEELS

BY CARL B. POST

### *Abstract*

*The preferred orientations existing in cold-rolled strip steel has been investigated by means of X-ray analysis. It is found that the "mean" orientation is specified by a [110] direction of the unit cell along the direction of rolling with a cube face tending to become parallel to the plane of rolling at high per cent reductions.*

*The diameter of the working-roll is shown to influence the angular deviation of the [110] direction from the rolling axis, that is, the smaller the working roll diameter the greater is the divergence of [110] from the rolling direction. No effect could be noticed on the dependence of the deviation of the cube face from the plane of rolling with roll size.*

*These results are discussed in the light of previous researches and are found to conform to the general picture of flow lines in metals.*

THE properties of rolled strip steel depend so markedly on the orientations of the metallic crystals that a study of the most probable orientations ("preferred orientations") under different conditions of rolling becomes of the highest importance. It is the purpose of this article to show the effect of the working roll diameter on the preferred orientation of crystals in cold-rolled strip steels. It will be shown that the diameter of the working rolls is much more important than the method used for applying power. In other words, it seems that there would be no outstanding difference between the preferred orientations produced by a Steckel type mill over that produced by an ordinary tandem mill if the roll diameters could be made the same.

### EXPERIMENTAL AND X-RAY TECHNIQUE

Samples were taken from tandem mill coils by stopping a tandem

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The author, Carl B. Post, Department of Physics, School of Chemistry and Physics, The Pennsylvania State College; formerly Assistant to the Metallurgist, Weirton Steel Corporation. Manuscript received February 12, 1936.

mill in operation and obtaining strips from the coil between the various stands. The tandem mill was of the conventional type of 4 stands of 4-high mills. Two sets of working rolls were used on the tandem mill, one of 19½ inch diameter, the other of 12 inch diameter. The Steckel mill used rolls 5½ inches in diameter. Samples were taken near the end of the coil where it enters the reelers, thus enabling samples to be cut of varying thicknesses. All the samples are listed in Table I. Figs. 1, 8, and 12, show that the original un-

Table I  
Listing of Samples for this Investigation

Sample Number		Roll Diameter and Type of Mill	Per Cent Reduction
1-1	Fig. 1	19½" Rolls, Tandem Mill	0% Hot Roll Coil, .072" thin
1-2	Fig. 2	same	42%
1-3	Fig. 3	same	64.6%
1-4	Fig. 4	same	81%
1-5	Fig. 5	same	88%
1-5	Fig. 6	same	X-ray beam "along" RD
1-5	Fig. 7	same	X-ray beam normal to sheet
2-1	Fig. 8	12" Rolls, Tandem Mill	0% Hot Roll Coil, .078"
2-3	Fig. 9	same	52%
2-4	Fig. 10	same	75%
2-5	Fig. 11	same	85%
4-1	Fig. 12	5½" Rolls, Steckel Mill	0%
4-2	Fig. 13	same	62%
4-3	Fig. 14	same	80%
4-4	Fig. 15	same	86%
5-1	Fig. 16	same	93% Final pass from a coil .082" thick reduced to .006"

rolled metal was substantially free from preferred orientation. Figs. 2-7, 8-11, and 12-17 are diffraction patterns of sample taken after rolling.

The X-ray technique was concerned with the following questions; (1) Evidence of the existence of preferred orientation and its nature; (2) A comparison of the degree of preferred orientation for different working-roll diameters; (3) Evidence of difference between the preferred orientation produced by the tandem and Steckel Mills.

Inasmuch as the samples as they came from the rolls were too thick to permit the obtaining of fiber diagrams by the conventional method in which the X-ray beam passes through the sample, diffraction patterns of such samples<sup>1</sup> were obtained by the "reflection" method and analyzed by the method of Post (1)<sup>2</sup>. In the reflection

<sup>1</sup>It is a pleasure to express appreciation to Dr. Victor Hicks of the University of Pittsburgh for his co-operation in taking the diffraction patterns, reproduced here as Figs. 1 through 16, while the writer was with the Weirton Steel Corp.

<sup>2</sup>The figures appearing in parentheses pertain to the references appended to this paper.

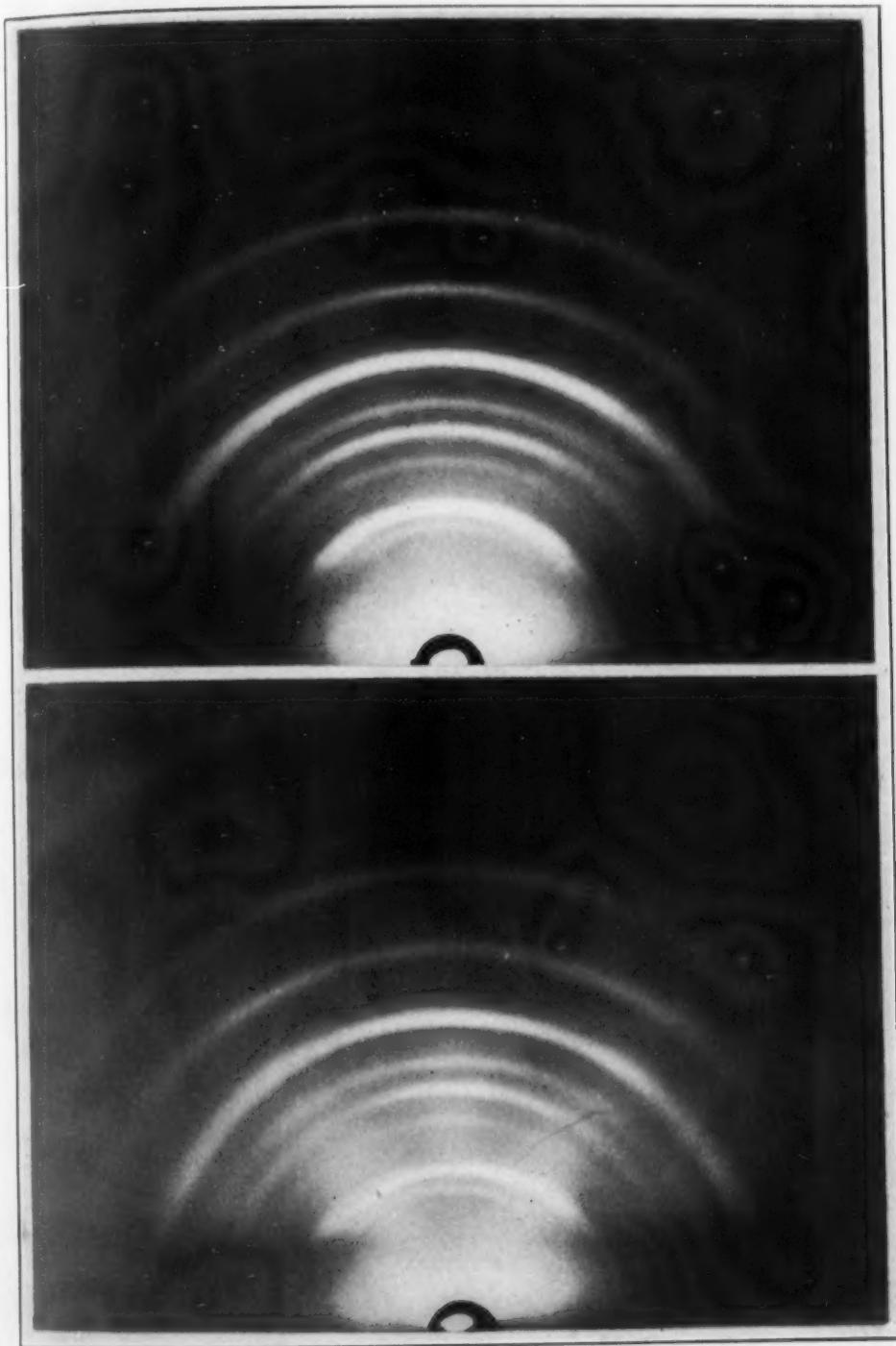


Fig. 1—Diffraction Pattern of Sample (1-1) Tandem Mill. 0.0 Per Cent Reduction. X-ray Beam "Across" R.D.  
Fig. 2—Diffraction Pattern of Sample (1-2) Tandem Mill. 42.0 Per Cent Reduction. X-ray Beam "Across" R.D.

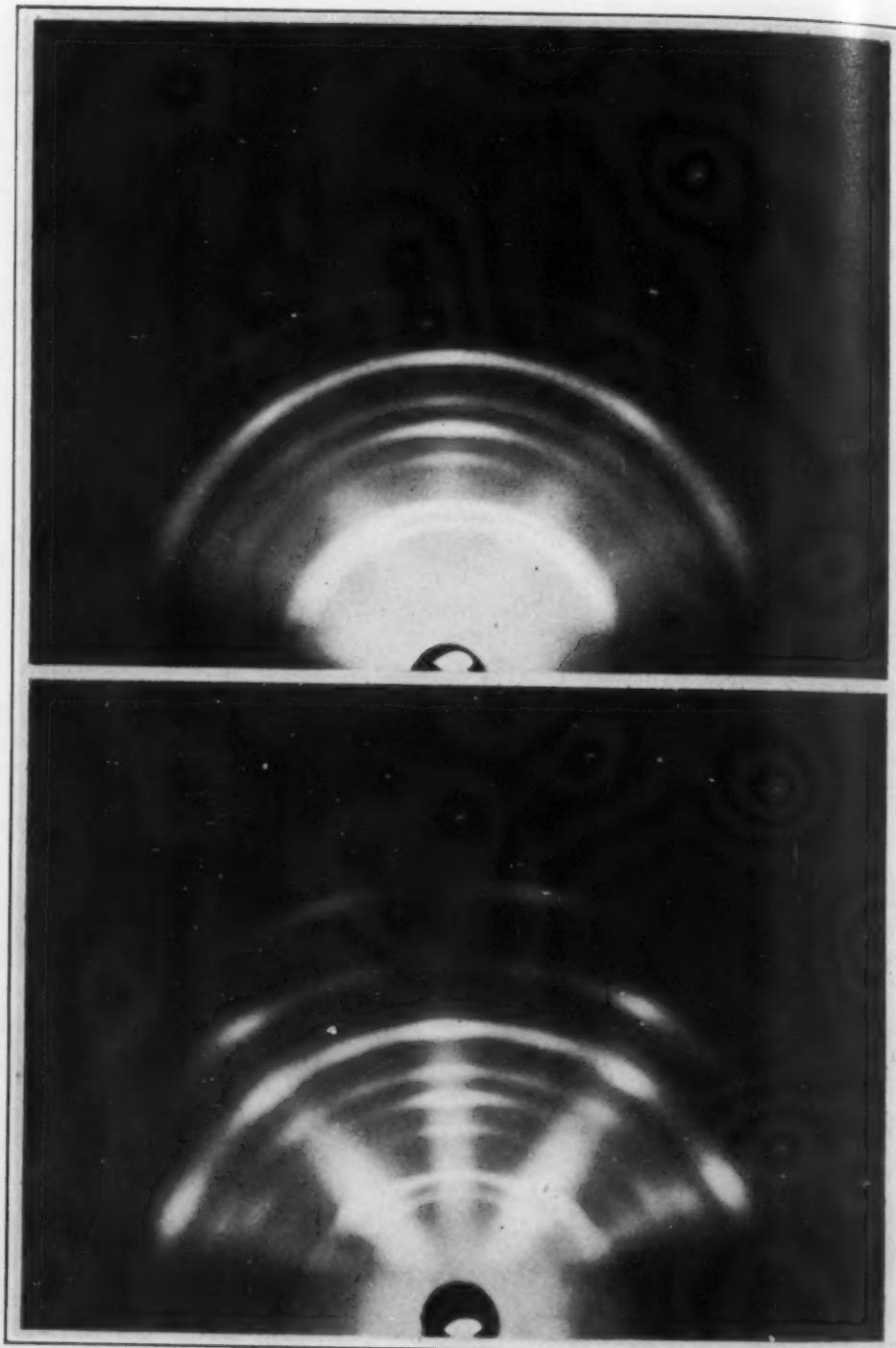


Fig. 3—Diffraction Pattern of Sample (1-3) Tandem Mill. 64.6 Per Cent Reduction. X-ray Beam "Across" R.D.  
Fig. 4—Diffraction Pattern of Sample (1-4) Tandem Mill. 81.0 Per Cent Reduction. X-ray Beam "Across" R.D.

method the plane of the sample is inclined at a small angle to the X-ray beam, and the diffracted rays are recorded on a photographic film placed, in these experiments, 5 centimeters from the center of the specimen on the opposite side of the specimen from the incident beam. The angle of inclination of the plane of the specimen to the X-ray beam varied between 6 and 8 degrees. This variation was necessary to avoid as much cold work as possible in straightening the samples. The 2-degree error thus introduced is well within the ordinary error of the interpretation of the X-ray data. Unfiltered molybdenum radiation was passed through a set of pinhole apertures which limited the angular beam divergence to about 3 degrees. With X-ray tube operating at 60 KV and 35 MA, exposure time was 90 minutes.

The diffraction patterns were chiefly made with the beam impinging on the sample "across" the direction of rolling, but several were made with the beam "along" the rolling direction, these latter being used to check the orientation about the axis of rolling. Diffraction patterns were also made with the X-ray beam strictly parallel to (a) the normal to the sheet (N.D.), and (b) the transverse direction (T.D.). The sample used in preparing diffraction patterns of type (a) (see Fig. 7) was etched to a thickness of 0.1 millimeter in nitric acid diluted with alcohol. The samples were fastened with beeswax to surfaces perpendicular or parallel to the X-ray beam.

#### DIFFRACTION PATTERNS AND TYPE OF PREFERRED ORIENTATION

The method of transposing the spots from the film to a stereographic projection net is given elsewhere and will not be repeated here (2), (3). The diffraction patterns for the three different roll diameters are shown in Figs. 1 through 16. Figs 1 to 7 show the patterns belonging to the 19 $\frac{1}{4}$  inch; Figs. 8 to 11 those belonging to the 12-inch working-roll diameter tandem mill; Figs. 12 to 16 show the diffraction patterns of the 5 $\frac{1}{4}$ -inch Steckel mill. In all of these patterns the preferred orientation contains a [110] direction along the direction of rolling with the additional limitation, at high reductions, of a cube face tending to become parallel to the plane of rolling. This is consistent with well known data already in the literature. The interest in the present work lies, therefore, not in the *type of orientation*, but in the *degree of orientation*. The following analysis of one series of patterns (the pattern belonging to a 19 $\frac{1}{4}$ -inch roll diameter, series 1-1, 1-2, etc.) will illustrate how to obtain quantitative values of the parameters specifying the orientation.

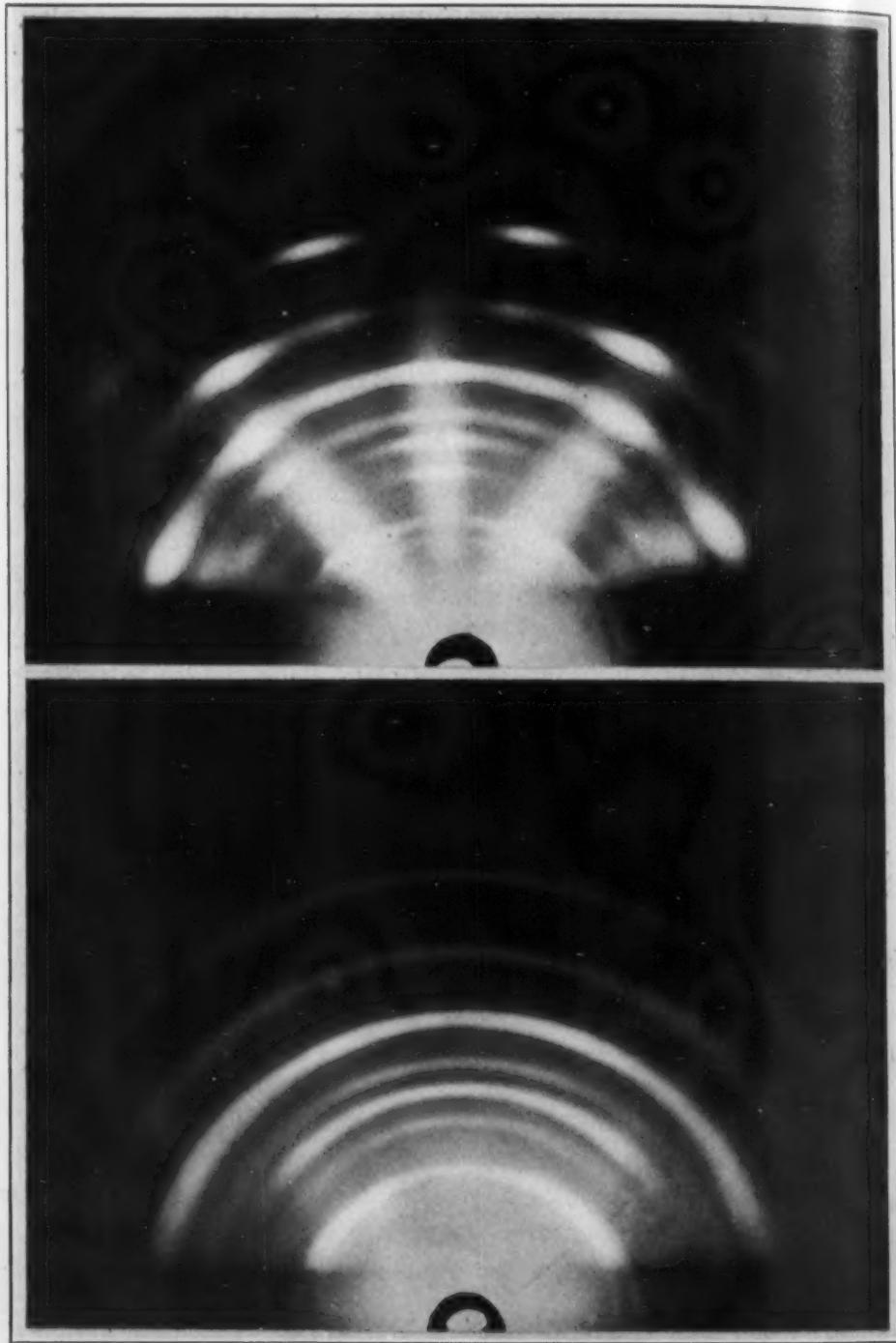


Fig. 5—Diffraction Pattern of Sample (1-5) Tandem Mill. 88.0 Per Cent Reduction. X-ray Beam "Across" R.D.

Fig. 6—Diffraction Pattern of Sample (1-5) Tandem Mill. 88.0 Per Cent Reduction. X-ray Beam "Along" R.D.

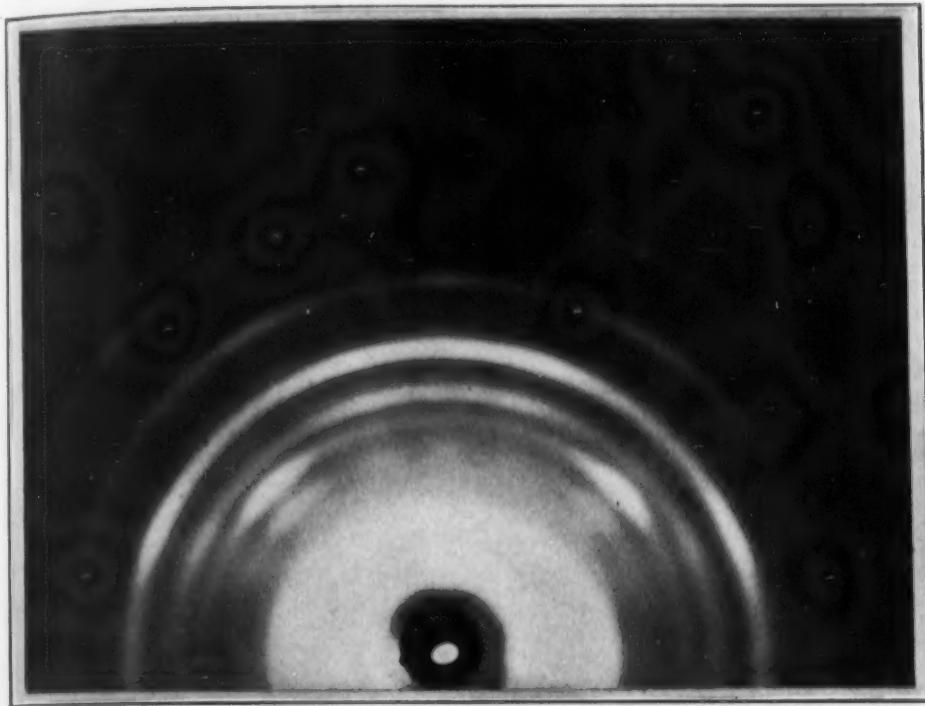


Fig. 7—Diffraction Pattern of Sample (1-5) Tandem Mill. 88.0 Per Cent Reduction. X-ray Beam Parallel to Sheet Normal.

Figs. 5 and 7 show the diffraction patterns made from sample 1-5 which had 88 per cent reduction in the tandem mill. Figs. 5 and 6 were made with the X-ray beams respectively "across" and "along" the rolling direction. Fig. 7 was made with the X-ray beam normal to surface of the sheet, i.e., perpendicular to both rolling and transverse direction. Fig. 1h (not shown here)<sup>3</sup> was made with X-ray beam perpendicular to both the normal and the rolling directions, i.e., parallel to the transverse direction. The arcs of the {310} rings from Figs. 1, 6 and 7 are reproduced to scale in Figs. 18b, 18c and 18d. The stereographic projection of the planes which give rise to these arcs is shown in Fig. 18a. Similar statements apply to Figs. 19, 20 and 21. These stereographic projections show that the crystals are oriented about a mean position which may be described by saying that the [110] direction of the elementary cube lies along the direction of rolling, and that a cube face lies parallel to the plane of rolling. The lengths of the arrows indicate the angular deviation of these normals when rotated about [110] as an axis and when rotated

<sup>3</sup>Fig. 1h, made with the beam perpendicular to both the normal and rolling directions represented only a rotation of 6 degrees from the figures labeled "across." As the spots were of the same position and intensity as Fig. 5, no advantage is lost by this omission.

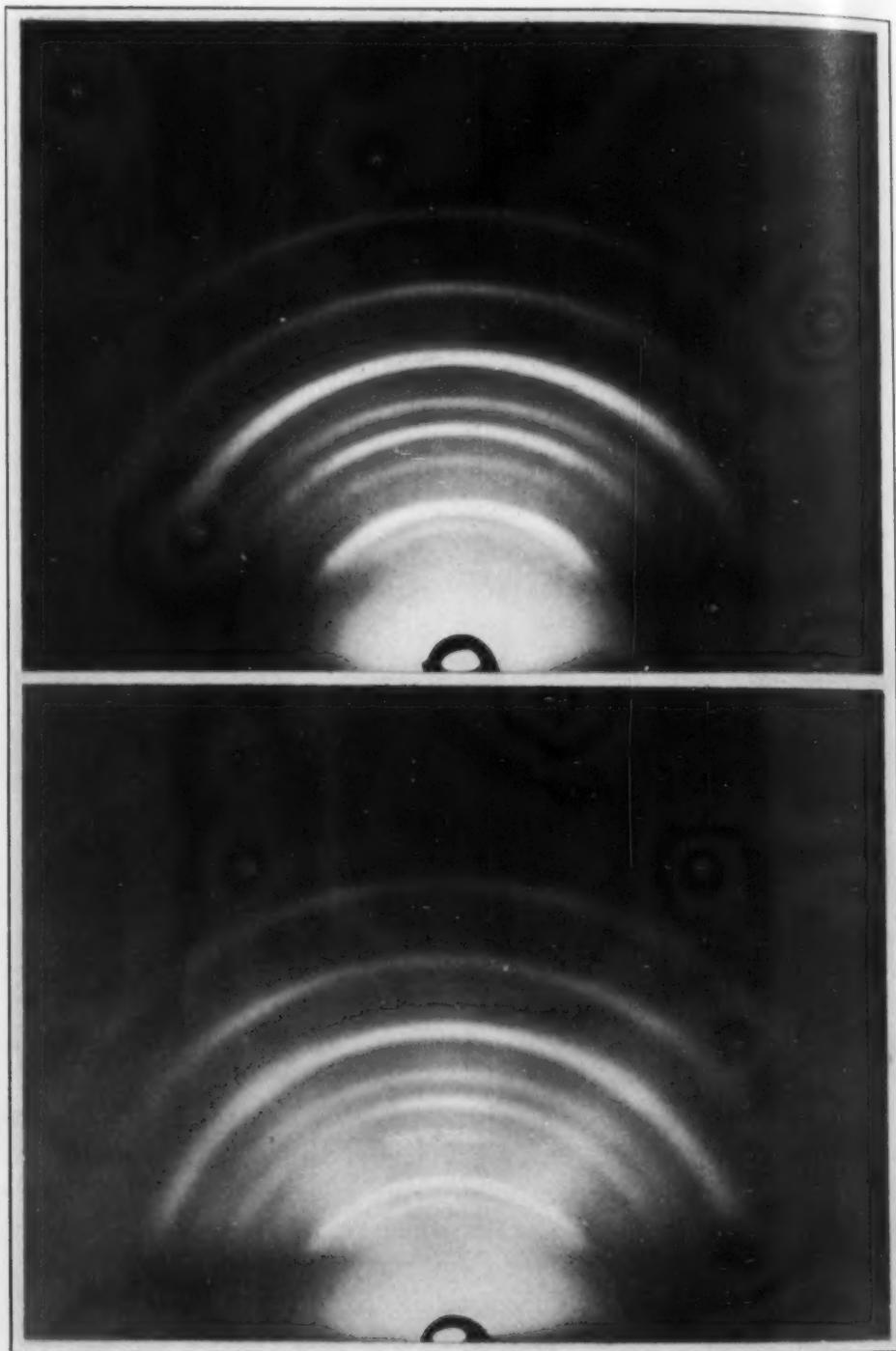


Fig. 8—Diffraction Pattern of Sample (2-1) Tandem Mill. 0.0 Per Cent Reduction. X-ray Beam "Across" R.D.

Fig. 9—Diffraction Pattern of Sample (2-3) Tandem Mill. 52.0 Per Cent Reduction. X-ray Beam "Across" R.D.

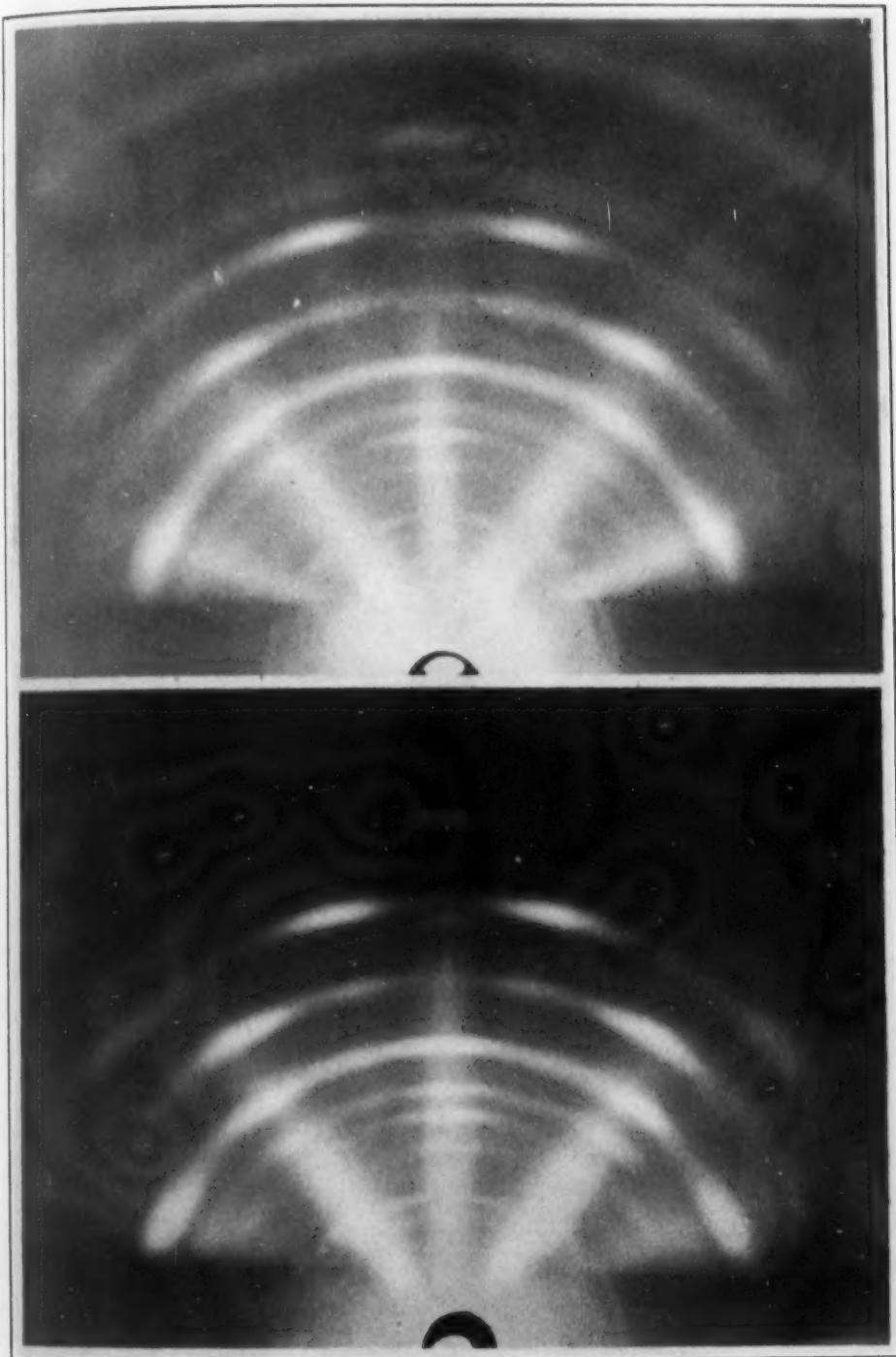


Fig. 10—Diffraction Pattern of Sample (2-4) Tandem Mill. 75.0 Per Cent Reduction. X-ray Beam "Across" R.D.

Fig. 11—Diffraction Pattern of Sample (2-5) Tandem Mill. 85.0 Per Cent Reduction. X-ray Beam "Across" R.D.

about a perpendicular to this direction. The latter deviation indicates the angular spread of the [110] direction from the rolling direction. The lack of complete pole-figure data is justified by the fact that the purpose of the present work can be attained with the data presented here.

The angular deviation of a [001] direction from the sheet normal may be determined as follows: The {310} family of planes offers a good reference group to check any rotation of the cube about the rolling direction. On the patterns obtained with the X-ray beam impinging across the direction of rolling and making 6 degrees of angle with the transverse direction, two spots (on one-half of the ring, or one quadrant) first make their appearance on the pattern 1-2 (Fig. 2), corresponding to a 42 per cent reduction. The ring keeps its unbroken appearance between spots in the case of the 65 per cent reduced sample (Fig. 3), but is clearly cut into definite segments (arcs), on the 81 per cent pattern (Fig. 4). As shown (Fig. 8), by the projection of the normals to the {310} planes and their paths belonging to a complete rotation of the cube about the [110] direction when this axis lies along the direction of rolling, a complete rotation of the cube should give rise to 4 spots per quadrant of the (310) type. These would appear at 75, 60, 45, and 30 degrees. The absence of the 60-degree spot on the (310) ring of Fig. 5 shows that the angle of lateral rocking must be equal to, or less than  $\pm$  60 degrees. This angle is sufficient to prevent the [130] direction (Fig. 18a) from attaining the proper angle for diffraction in the case of the "across" pattern (Fig. 18b). With this information we may take  $\pm$  60 degrees as the angle of lateral rocking and draw the arrows belonging to the normals in the {110}, {100}, and {211} families. These are shown in Figs. 19, 20 and 21. The disappearance of spots on the various rings, due to this limited rotation, is clearly brought out by the accompanying schematic drawings of the patterns, viz. Figs. 18b, 18c and 18d, etc.

As shown by these patterns, it is highly probable that a complete "fiber" diagram for commercially rolled strip is rarely attained. It would follow from the patterns of Figs. 1 through 16, that the cube is rotated about the [110] direction as an axis, but not in the sense of complete random rotation. In view of the mechanism of rolling, which we know to exert only very small forces in a transverse direction with reference to the rolling direction, we must assume that the angle of rotation about this axis steadily decreases

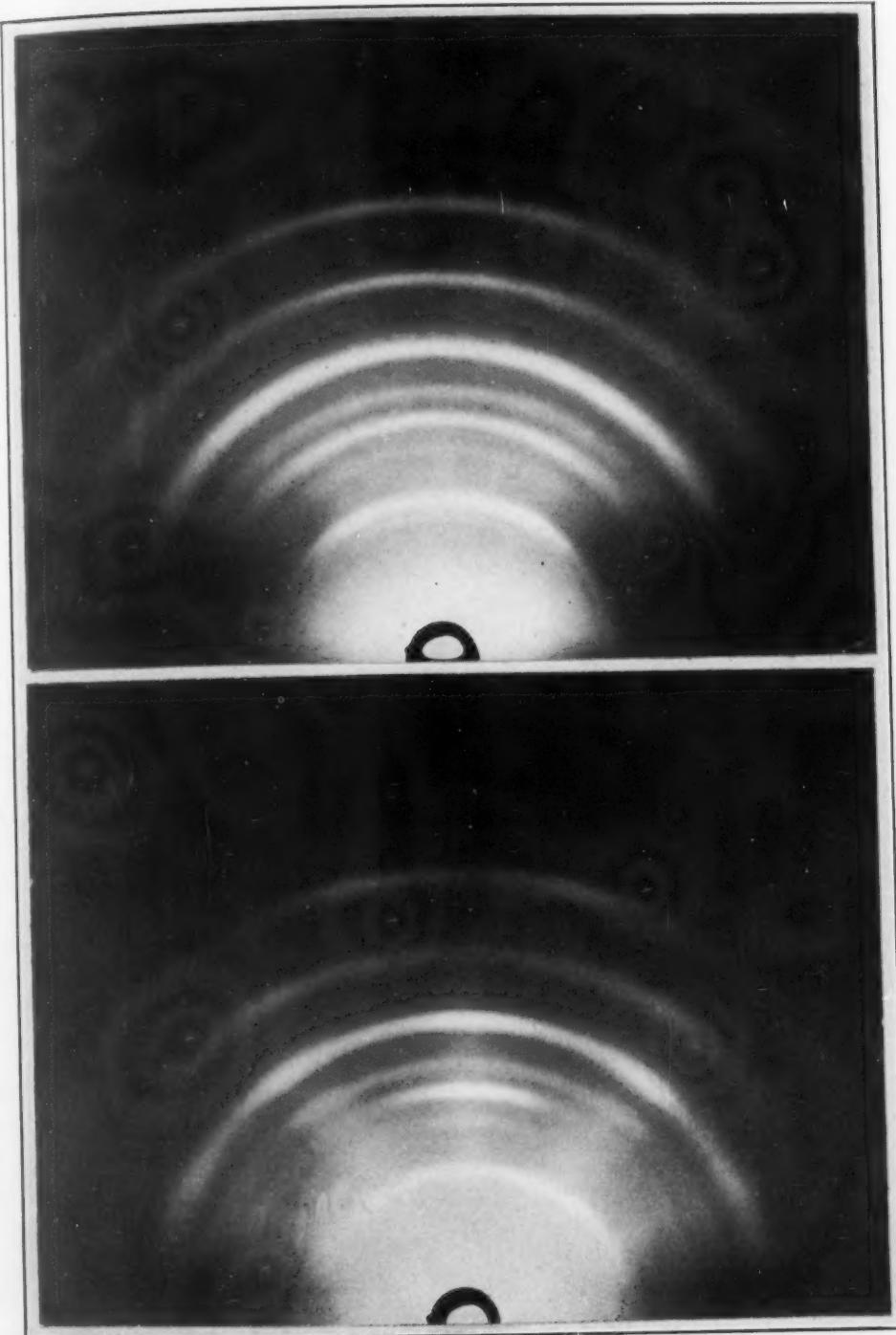


Fig. 12—Diffraction Pattern of Sample (4-1) Steckel Mill. 0.0 Per Cent Reduction. X-ray Beam "Across" R.D.

Fig. 13—Diffraction Pattern of Sample (4-2) Steckel Mill. 62.0 Per Cent Reduction. X-ray Beam "Across" R.D.

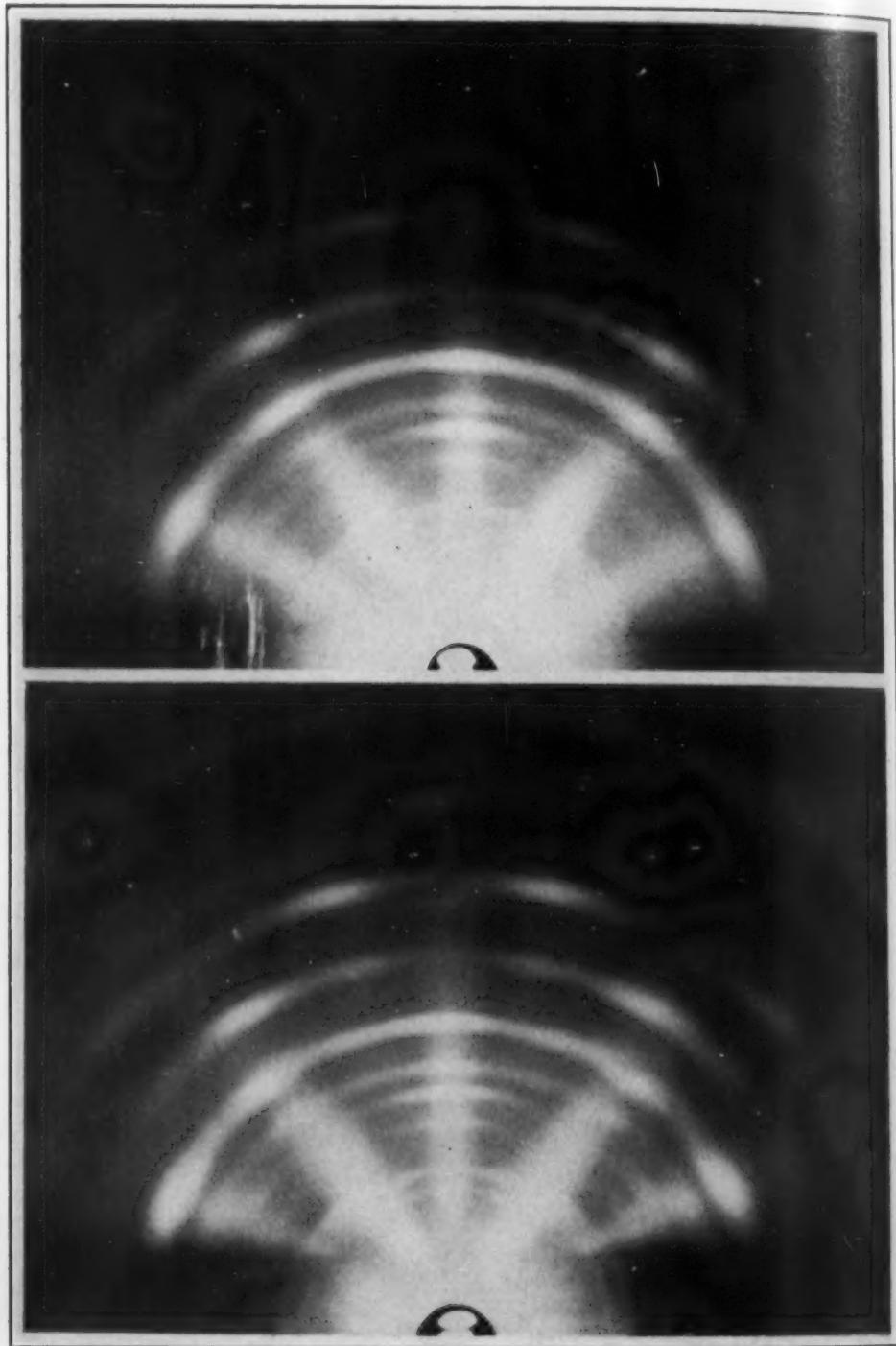


Fig. 14—Diffraction Pattern of Sample (4-3) Steckel Mill. 80.0 Per Cent Reduction. X-ray Beam "Across" R.D.

Fig. 15—Diffraction Pattern of Sample (4-4) Steckel Mill. 86.0 Per Cent Reduction. X-ray Beam "Across" R.D.

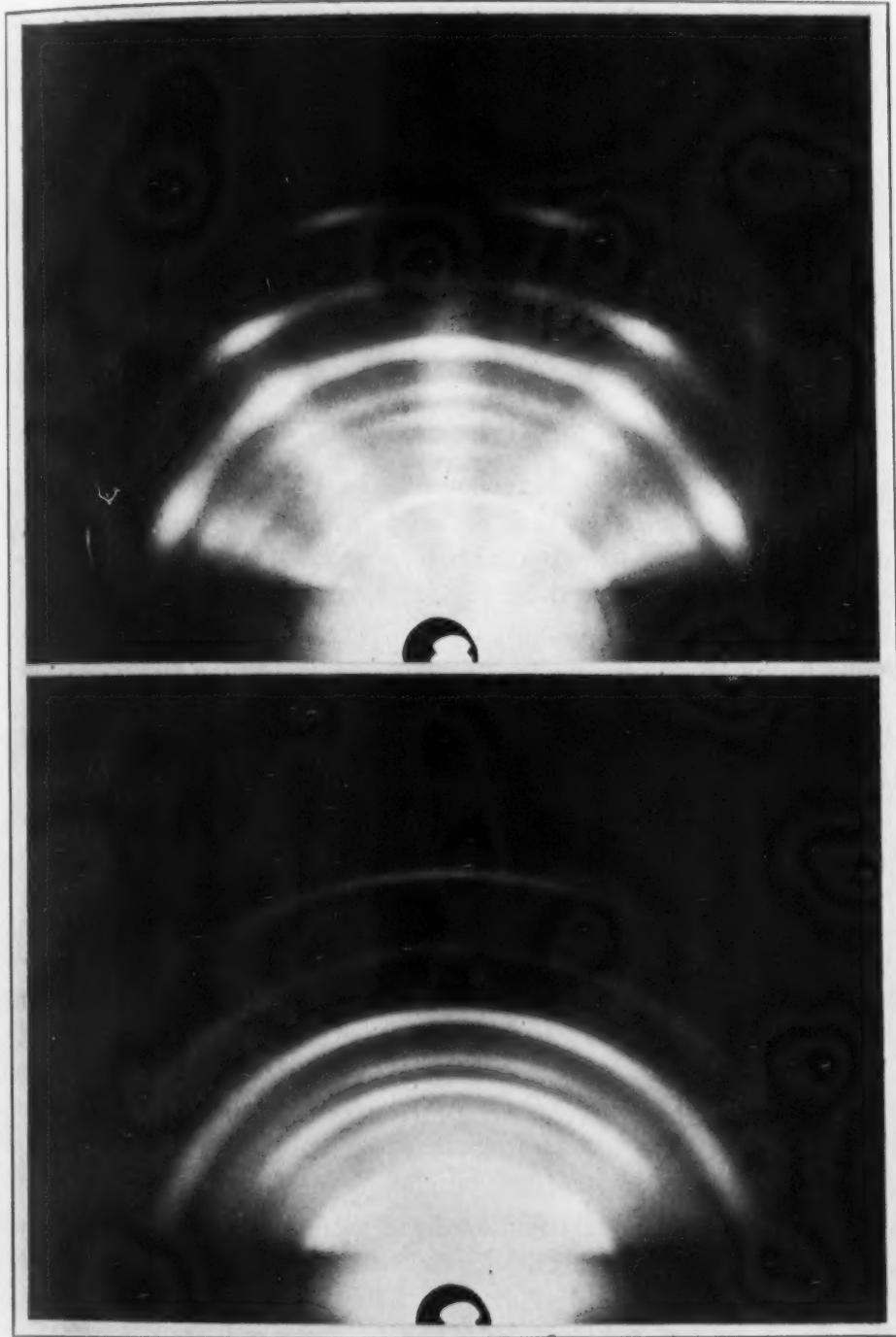


Fig. 16—Diffraction Pattern of Sample (5-1) Steckel Mill. 93.0 Per Cent Reduction. X-ray Beam "Across" R.D.

Fig. 17—Diffraction Pattern of Sample (5-1) Steckel Mill. 93.0 Per Cent Reduction. X-ray Beam "Along" R.D.

Table II  
Angular Spread of 90° Spot, (100)-Ring

Per Cent Reduction	Degree Spread
19 1/4-Inch Roll	0
Diameter	42
Tandem Mill	74.6
	81
	88
	15 - 16
12-Inch Roll	0
Diameter	52
Tandem Mill	76
	85
5 1/4-Inch Roll	0
Diameter	62
Steckel	80
	86
	93
	17

as the per cent reduction is increased. Figs. 18a and 18b show that in the case of the 88 per cent reduced sample, the angle of rotation about the [110] axis is approximately  $\pm 60$  degrees. The diffraction patterns of sample 1-5, Fig. 7, taken with the beam strictly normal to the plane of rolling checks this rotation for the 88 per cent reduced sample. Two spots appearing at 60 and 45 degrees, and the absence of spots at 75 degrees and close to the direction of rolling clearly follow from the stereographic projection belonging to the {310} family in Fig. 18a.

The angle of deviation of the [110] direction from the direction of rolling is computed from the angular spread of the spots appearing on the various arcs. This was found to range from  $\pm 20$  to  $\pm 13$  degrees in the case of reductions ranging from 42 to 65 per cent and  $\pm 13$  to  $\pm 7$  degrees for reductions ranging from 65 to 88 per cent. These angles will be discussed later with reference to difference in orientation existing between the various samples.

#### PREFERRED ORIENTATION AS A FUNCTION OF ROLL DIAMETER

The angular spread of the 90-degree spot in the {100} ring as a function of per cent reduction is shown in Fig. 22. From the graphs for the 19 1/4-inch and 12-inch diameter rolls of the tandem type of mill, it is clearly evident that the diameter of the working rolls has a noticeable effect upon one of the parameters specifying the orientation. From these two graphs it would be easy to estimate about what the effect would have been of 5 1/4-inch rolls in a tandem type mill. Fig. 22 shows that such an estimated effect is not

far from that found experimentally for the  $5\frac{1}{4}$ -inch rolls of the Steckel mill. Before discussing these results from the standpoint of theory, it will be necessary to point out certain sources of error in some of the literature.

As pointed out by Wever (4) considerable disagreement is encountered in the literature when the effect of rolling variables are

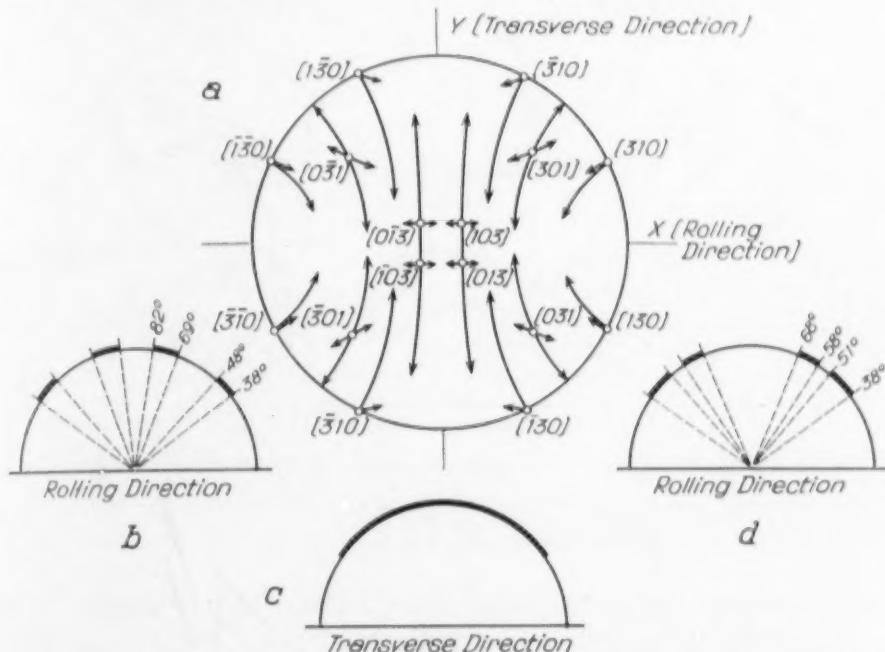


Fig. 18a-18d—Stereographic Projection of Range of Orientations Belonging to the {310} Family of Planes.  
 Fig. 18b—Arcs of the (310)—ring from Fig. 5.  
 Fig. 18c—Arcs of the (310)—ring from Fig. 6.  
 Fig. 18d—Arcs of the (310)—ring from Fig. 7.

considered. Part of the disagreement is due to the methods of rolling the metal, initial grain-size, and chemical analysis, but some is due to faulty conclusions derived from an X-ray study of the rolled samples. Most of the X-ray methods used are not very sensitive to changes in orientation, and consequently are to be used only as a tool for the physical metallurgist, and in case of ambiguous results should be interpreted in accord with common metallurgical experience. Some of this uncertainty in results is due to placing too great a confidence in diffraction patterns obtained by having the samples only perpendicular and normal to the incident X-ray beam. Such a method gives only a few diffraction rings, principally the {110}, {100}, and {211}, and if the radiation is made monochromatic by

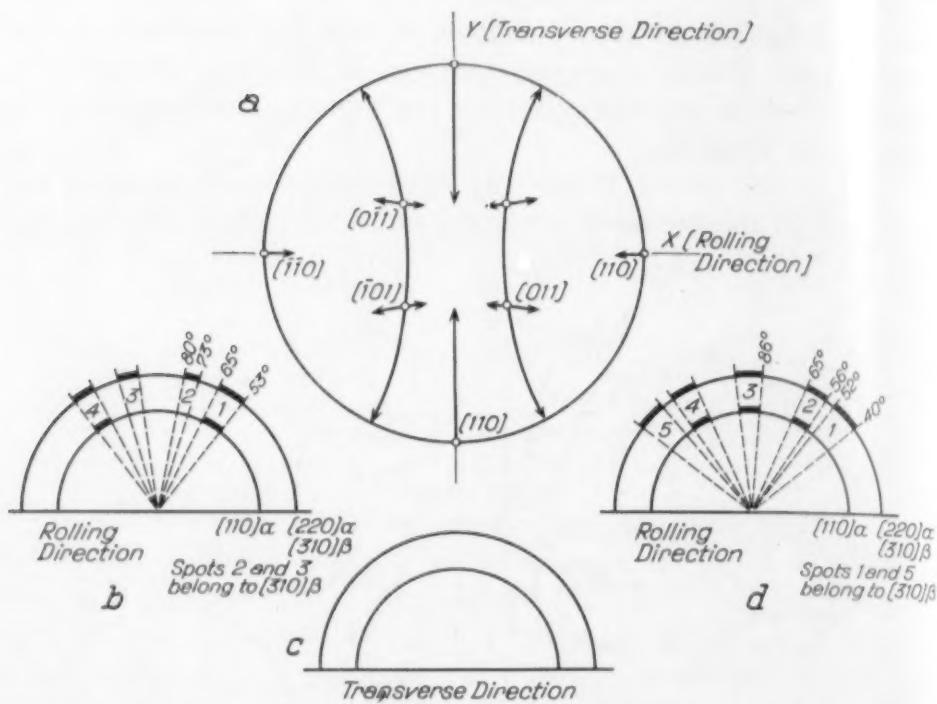


Fig. 19a-19d—Stereographic Projection of Range of Orientations Belonging to the 110 Family of Planes.  
 Fig. 19b—Arcs of the (110)—ring from Fig. 5.  
 Fig. 19c—Arcs of the (110)—ring from Fig. 6.  
 Fig. 19d—Arcs of the (110)—ring from Fig. 7.

strong filtering, the intensity of these latter rings is usually so reduced as to make measurements difficult.

It is frequently found in the literature that the so-called "six-point" and "four-point" pattern, i.e., the number of localized spots on the band caused by white radiation diffracted from the {110}-family is used as a criterion for determining whether a "fiber" or "limited" type of orientation exists. An inspection of Fig. 19a shows the fallacy in these interpretations. In order that the (011) planes may show a spot between 0 and 90 degrees on an N.D. diffraction pattern (Mo rays) (Fig. 7), the angle of rotation about [110] as an axis must exceed  $\pm 35$  degrees. This spot and the spot at 90 degrees, when symmetrically repeated over 360 degrees, would give a "six-point" pattern. All angles less than this would result in the appearance of a "four-point" pattern. The method will give consistent results when the angle of rotation is less than  $\pm 35$  degrees, but as ordinarily used, a rotation greater than 35 degrees but less than 90 degrees, cannot be interpreted with any degree of precision.

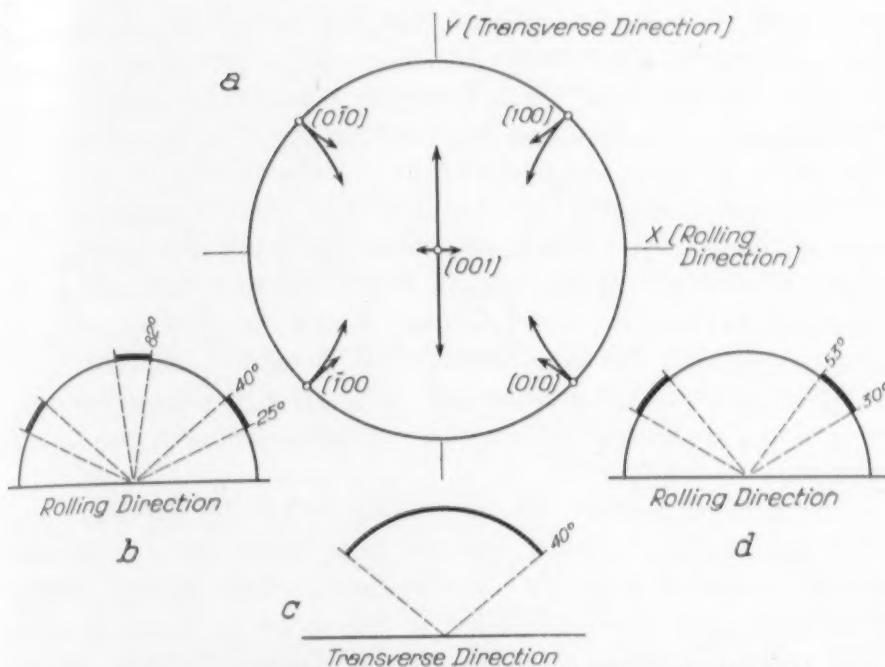


Fig. 20a-20d—Stereographic Projection of Range of Orientations Belonging to the 110 Family of Planes.  
 Fig. 20b—Arcs of the (110)—ring from Fig. 5.  
 Fig. 20c—Arcs of the (110)—ring from Fig. 6.  
 Fig. 20d—Arcs of the (110)—ring from Fig. 7.

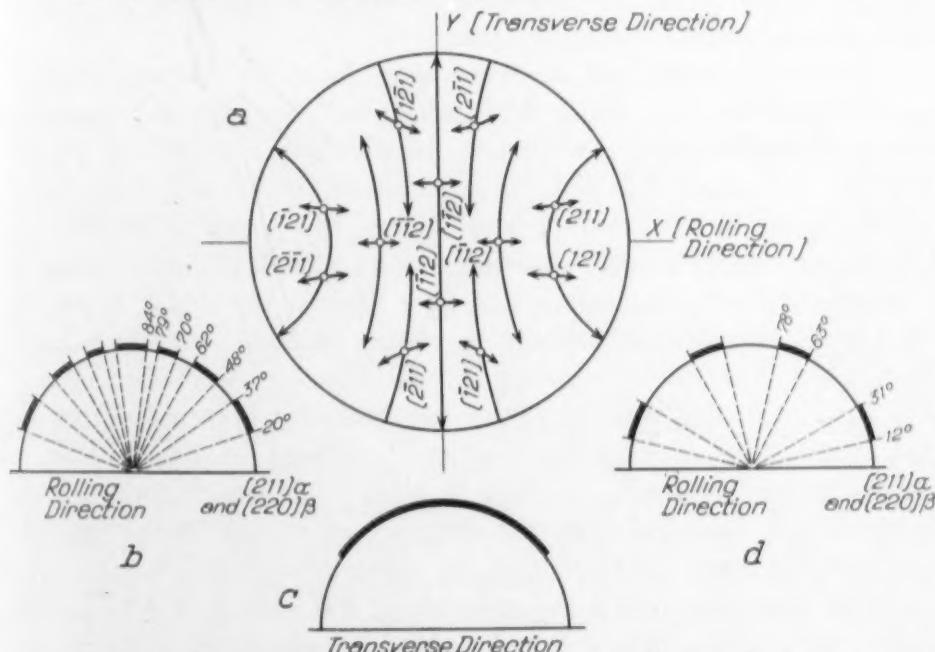


Fig. 21a-21d—Stereographic Projection of Range of Orientations Belonging to the 211 Family of Planes.  
 Fig. 21b—Arcs of the (211)—ring from Fig. 5.  
 Fig. 21c—Arcs of the (211)—ring from Fig. 6.  
 Fig. 21d—Arcs of the (211)—ring from Fig. 7.

Norton (5) has considered the degree of two-dimensional changes in plastic deformation and their effect upon the preferred orientation produced thereby. From his conclusions, if the change in reduction in one direction far exceeds the change in reduction in the other direction, the preferred orientation will be nearly exact. From this it is concluded that the type of preferred orientation in a cold-worked material depends only upon the particular process employed. However, it is well known that different commercial methods of cold working the material, even though the different methods give approximately the same dimensional changes, give very different degrees of preferred orientations. Accordingly, Norton considers these changes to be due to frictional conditions between the surface of the sheet and roll.

The modern method of cold rolling, either by the tandem or Steckel process, represents a decrease in friction between the metal and rolls compared with the older methods. The smaller working roll diameters and tension applied to the metal in the case of the Steckel mill, all combine to reduce the roll friction. Siebel (6) has developed a method of graphical analysis for the effect of roll diameter and the coefficient of friction between the metal and rolls on the rolling pressures, but this theory cannot be extended to predict the preferred orientation at present.

The two tandem roll diameters considered here have the same coefficient of friction, about 0.25, while the Steckel mill rolls have this coefficient reduced considerably to a value in the neighborhood of 0.15. Although it is possible to attribute the results found here to this coefficient of friction, nevertheless, the writer is inclined to believe that the differences in orientations found here are principally a function of roll diameters. The flow lines in the metal, as rolled on a small diameter roll, should be steeper than the flow lines in a sheet which was rolled by a larger roll. This condition is pictured in Fig. 23. In this way we preserve a unified concept of deformation from a roll of infinite diameter (pressing) to a roll of very small diameter (drawing through a die). The greater divergence of the [110] direction from the direction of rolling in the case of smaller roll diameters would seem to substantiate this concept.

The least rotation of the cube about the rolling direction, i.e., about [110], as an axis is found to be approximately  $\pm 55$  degrees in this work. This corresponds to a reduction of 88 per cent, (Samples 1-5, 5-1, and 2-4), and there is indication that this angle of

lateral rocking decreases rapidly with reductions over 90 per cent. As was shown before, the patterns of reductions less than 75 per cent indicate that even here the rotation is not random about this axis. The point that should be emphasized, however, is that by the

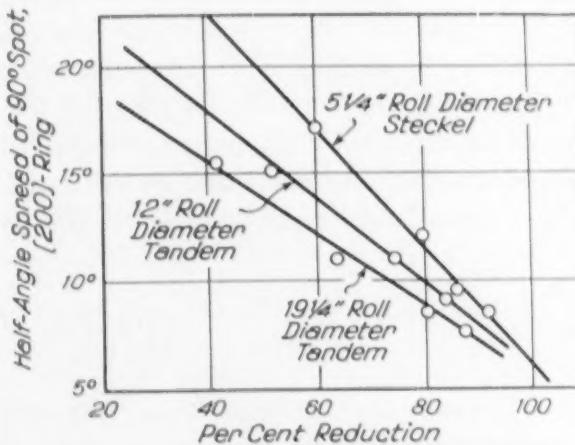


Fig. 22—Angular Spread of 90-Degree Spot, (100)-ring as a Function of Per Cent Reduction and Roll Diameter. Half of this Spread Represents very Closely the Deviation of [110] from the Rolling Direction.

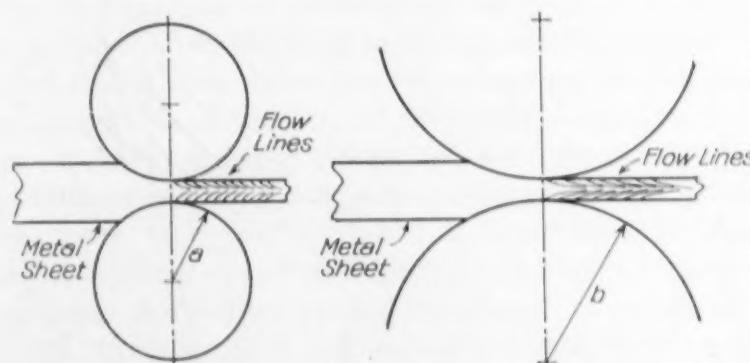


Fig. 23—Supposed Direction of Flow Lines Due to Rolls of Different Diameters.

criterion of a "six-point" or "four-point" pattern, cold-rolled strip steel would have a random rotation of the cube about the rolling (i.e., the [110]) direction until reductions in the neighborhood of 90 per cent or more are reached. As shown here this result cannot be true, but is to be modified so that the random rotation of the cube about this axis decreases steadily with increasing per cent reduction above 40 per cent to about 85 per cent and then decreases rapidly for reductions over 90 per cent. Within the limits permitted by the roll diameters available in this work, the roll diameter has only a

negligible effect on the angle of rocking about the rolling direction, i.e., about [110].

Roll diameter has a pronounced effect, however, on the angle of rocking about the transverse direction, i.e. about [110]. As mentioned before, the half-angle spread of the 90-degree spot on the {110}-ring is approximately the deviation of the [110] direction from the rolling axis. From Fig. 22 it can be stated that the smaller the roll the greater is the angular deviation of the [110] direction from the rolling direction. At high reductions this effect becomes increasingly smaller, and the lines on the graph should converge to a common point in the neighborhood of 100 per cent reduction.

#### DIFFERENCE IN PREFERRED ORIENTATIONS PRODUCED BY THE TANDEM AND STECKEL MILLS

Although a difference does exist between the patterns belonging to tandem and Steckel mill rolling, the results shown here and the results of other researches tend to show that this difference is to be attributed almost entirely to the roll diameters used. This conclusion cannot be checked directly by using rolls of tandem mill diameter on a Steckel mill because of the experimental difficulties. Sisson (7) found that the application of tension below the elastic limit to the strip (this is the principle of the Steckel mill in driving the rolls by frictional contact with the coil which is being pulled through the mill) during the rolling process does not effect the establishment of final degree of preferment.

There is one feature of the diffraction patterns which may be due to the change in roll diameter or to the method of rolling. On comparing the tandem mill series 1-2, 1-3, etc., with the Steckel mill series 4-1, 4-2, etc., it is noticed, going backward in the series, that as the amount of reduction is decreased, the photographic contrast of the spots relative to the adjacent parts of the continuous rings is decreased. This phenomenon is more marked than the numerical changes in the half arc lengths. It indicates that, while an appreciable degree of preferred orientation is obtained with moderate reductions, there is still a large number of crystallites with random orientation. A comparison of the two samples with 62-65 per cent reduction is interesting from this viewpoint. While the spots are longer on the diffraction of the Steckel mill sample 4-2, than that of the tandem mill sample 1-3, they are blacker relative to the continu-

ous rings (i.e., whiter on the prints). Thus, while the tandem mill sample shows a higher degree of perfection of the preferred orientation at this reduction, it leaves a larger fraction of the crystallites with a random orientation. How much of this is due to the roll diameter and how much to the method of rolling cannot be said at the present time.

### CONCLUSIONS

From the results of this work several definite conclusions may be drawn as to the effect of working-roll diameter on the degree of orientation obtained in cold-rolled strip steel products:

(a) In all cases of roll diameters considered here, and in both cases of the two types of rolling strip steel, viz., the tandem and Steckel mill, the preferred orientation can be specified by having a [110] direction of the unit cell of the iron crystallites along the direction of rolling and a rotation of the cube about this direction as axis. This rotation is not completely random about this axis, but, starting with reductions in the neighborhood of 40 per cent, the angle of rotation steadily decreases to about  $\pm 55$  degrees in the neighborhood of 85 to 90 per cent reduction. Above this point the angle of lateral rocking should decrease very fast with increasing per cent reduction. The angle of deviation of the [110] direction from the direction of rolling is found to be a function of the per cent reduction and will decrease steadily with increasing reduction. This was found to be approximately 20 degrees for the samples of 40 per cent reduction and 7 degrees for the samples of about 90 per cent reduction.

(b) The angle of deviation of the [110] direction has been shown to be definitely a function of the working-roll diameter. This means that for any given per cent reduction, the smaller working roll will produce a preferred orientation which has a larger angle of deviation of the [110] direction from the rolling axis than the orientation obtained with a larger roll. A change in the angle of lateral rocking with roll diameter could not be detected in the present work.

(c) The differences existing in the preferred orientation made by the Steckel and tandem type mills has been shown to be due principally to differences in roll diameters and not to the method of driving the mills. In other words, as long as the tension is below the elastic limit of the steel, the application of tension to the sheet

does not seem markedly to influence either the type or the degree of preferred orientation found in the cold-rolled strip. Although the tandem mill produces a higher degree of preferred orientation at low per cents of reduction, it seems to leave a larger fraction of the crystallites with random orientation than the Steckel. Whether this is due to the roll diameter effect, or to the method of rolling, cannot be decided at the present time.

(d) Obviously, the results presented here for low per cent reductions (45 to 60 per cent) of commercial strip coils for tin-plate gages will apply equally well to strip gages for auto-body use.

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## THE SODIUM CYANIDE METALLOGRAPHIC ETCH TEST FOR REVEALING PRECIPITATED CARBIDES IN THE 18-8 TYPE STAINLESS STEELS

By W. B. ARNESS

### *Abstract*

*Much of the attention devoted to the study of the 18-8 type stainless steels has been focused upon the related problems of carbide precipitation and intergranular corrosion. Methods of detecting the presence of carbides have been developed, and one of them — the sodium cyanide metallographic etch — has been found to be reliable and sensitive. Properly used it will reveal carbides without attacking austenite or crystal boundaries.*

*The test is applied to 18-8 in any condition, as after hot or cold working, after heat treating or welding, or after exposure to corrosive media. Specimens are polished, immersed in a ten per cent solution of NaCN in water, and electrolytically etched, in preparation for examination under the microscope, usually at  $\times 500$ . Carbides, when present, appear as black lines or globules in an otherwise unetched surface.*

*The principal objects of this study were to determine whether the NaCN test can be relied upon to reveal the presence of precipitated carbides in 18-8 steels, and to outline a satisfactory technique for applying it. Attention was also directed to consideration of the proper scope of the test, and a discussion of this aspect of the problem is included.*

*Typical results are illustrated in Figs. 1 to 24. All specimens were selected from commercial heats, and their treatment prior to testing was carefully supervised. All were anodically etched in the NaCN solution, using a six-volt current. The size and shape of the specimens varied a little, but usually they were approximately  $\frac{1}{2}$  inch square  $\times \frac{1}{8}$  inch to  $\frac{1}{4}$  inch thick. A distance of one inch, measured by eye, was maintained between the polished surface of the specimen and the parallel surface of the platinum cathode.*

### **RELIABILITY OF THE TEST FOR QUALITATIVE RESULTS**

**A** SATISFACTORY qualitative test for precipitated carbides in 18-8 steels might be defined as one that would give consistently

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The author, W. B. Arness, mill superintendent, Rustless Iron and Steel Corp., Baltimore Md. Manuscript received June 1, 1936.

negative results when applied to annealed specimens wherein all carbides are in solution, but which would infallibly reveal even the faintest traces of precipitated carbides when they are present.

To judge the efficacy of the NaCN test by these standards, many specimens, both high and low carbon, were examined. The appearance of a typical annealed structure, with all carbides in solution, is illustrated in Fig. 1. As expected, no carbides are revealed. Nor is any trace of the crystal structure in evidence. The result is, as it should be, completely and consistently negative.

In Fig. 6, the structure of a specimen heated for five minutes at 1200 degrees Fahr. (650 degrees Cent.) to bring about slight precipitation of carbides is shown. Here the carbides that were deliberately produced are clearly seen. Even when a very short exposure to carbide precipitation heating is involved, as by a simple welding of low carbon (0.05 per cent) plate, carbides are clearly revealed (Fig. 5). Examination of many specimens treated so as to induce carbide precipitation confirmed these typical results.

So far the NaCN test meets the requirements of our definition, but before finally endorsing it, several important questions remain to be answered:

1. Can the test be manipulated so as to reveal austenite boundaries, or any constituents other than precipitated carbides?
2. What result is obtained when the test is applied to 18-8 steels containing special supplementary elements?
3. How do results of the NaCN test compare with results of other metallographic tests used for the same purpose?
4. Can the test be used to measure quantitatively the amount or degree of carbide precipitation?
5. What is the effect of prior hot and cold treatment of the steel upon the appearance of carbides as revealed by the test?

1. *Selectiveness of the Test* — To determine whether the NaCN solution will etch austenite, many annealed specimens were examined, of which Figs. 2, 3 and 4 are typical illustrations. An annealed low carbon 18-8 steel containing some ferrite, or delta iron pools, was etched (Fig. 2). Although no trace of austenite appeared, the ferrite pools were quite clearly outlined. This is a typical result, but fortunately leads to no confusion, and does not reflect upon the use-

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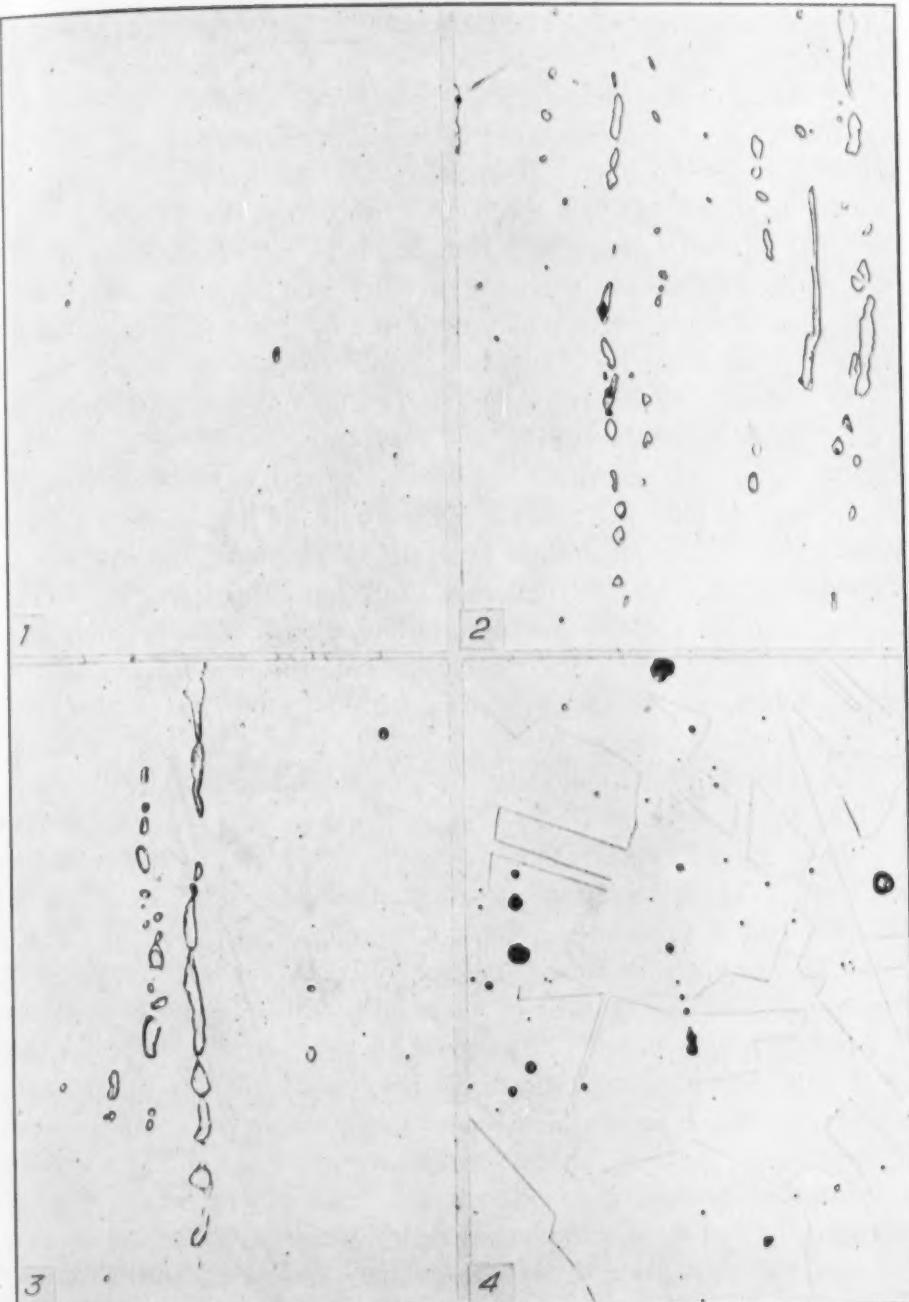


Fig. 1—Annealed, Etched 5 Min.—No Carbides. C 0.05, Cr 17.8, Ni 9.3.

Fig. 2—Annealed, Etched 5 Min.—No Carbides. Ferrite Pools Lightly Outlined. C 0.06, Cr 19.2, Ni 8.3.

Fig. 3—Annealed, Etched 20 Min.—No Carbides. Ferrite Pools More Heavily Outlined. C 0.05, Cr 19.5, Ni 8.3.

Fig. 4—Annealed, Etched 30 Min. Crystal Boundaries Are Finally Being Etched. Note Enlarged Pits. C 0.05, Cr 17.8, Ni 9.3. All Specimens Etched Electrolytically in NaCN—6 Volts.  $\times$  500.

fulness or reliability of the test, because ferrite is clearly recognizable as such.

Prolonging the etching period to twenty minutes, which is several times longer than required to reveal carbides, fails to bring out any constituents remotely resembling carbides (Fig. 3). The only effect is to slightly darken the boundaries of the ferrite pools.

It is not until the etching time has been increased to thirty minutes (Fig. 4) that the austenite structure begins to appear. Some pitting has also occurred, which is caused by removal of nonmetallics and enlargement of their cavities. Since there is no reason to etch for so long a time, this result has no practical significance, and is not a valid objection to the test.

*2. Effect of Addition Agents*—General experience with the NaCN reagent indicates that the presence of the usual addition agents in 18-8 alloys does not detract from its discriminating preference for carbides. Figs. 15 to 22 illustrate the reliability of the test for revealing carbides in 18-8 steels containing manganese, tungsten, molybdenum and titanium, and clearly indicate the similarity in appearance and behavior of carbides as measured by the NaCN test in all of these complex steels.

In refutation of the effectiveness of the NaCN test for studying carbide precipitation in 18-8 steels, it has been said that this reagent reveals carbides in other (than 18-8) rustless irons, and even in carbon steel. That it does, appears substantiated (Figs. 23 and 24), but this is hardly a valid reason for condemning application of the test to the 18-8 steels, providing it is kept in mind that the test makes no pretense of identifying each of these differently composed carbides.

It is strongly urged by makers and users of these special 18-8 steels that carbide precipitation may be so controlled in the presence of certain addition agents, which supposedly affect the composition or distribution of carbides, that susceptibility to intergranular corrosion is reduced or prevented despite the existence of carbides. It is not proposed here to discuss the question, but granting that there is some basis for this contention, it is obvious that the mere detection of carbides by the NaCN test is no criterion for judging the corrosion behavior of these steels.

*3. Results Obtained in Comparison with Results of Other Tests*—Several other metallographic tests have been used for detecting carbide precipitation. Of these, electrolytic etching with nitric acid, immersion etching with hydrochloric acid-ferric chloride solu-

tions, with Murakami's solution (potassium ferricyanide and sodium hydroxide) and with Vilella's reagent (aqua regia in glycerine) are most familiar. Recently electrolytic etching with oxalic acid has been proposed.

All of these methods may be used successfully by an experienced metallographist, but each has its own idiosyncrasies which must be thoroughly understood before reliable results can be obtained. For instance, etching electrolytically with  $HNO_3$  for thirty seconds suffices to develop the crystal structure of 18-8, whether or not carbides are present. Thus, use of this method relies upon preferential rapid etching of carbides when present, in a very few seconds, and halting the etching attack after carbides have been resolved, but before the structure itself has become visible. It is obvious that use of such a reagent requires considerable skill and judgment, and that it might frequently be doubtful whether apparent results are in fact what they seem.

Since the action of  $HCl-FeCl_3$  solutions and of Vilella's reagent are quite similar in that they, too, etch crystal structures in 18-8 after only a few seconds exposure, the same objections apply to their use for revealing carbides.

Murakami's reagent has been widely used, and possesses the advantage that it does selectively resolve carbides. Some investigators who prefer it obtain consistent and excellent results. However, four objections to it have been voiced, which seem to be based on good evidence:

1. Carbides are not always sharply outlined.
2. It is sometimes difficult to obtain uniform etching over the entire surface of the specimen.
3. There seems to be a tendency to underestimate the severity of precipitation.
4. Results are wholly untrustworthy unless the polishing of the specimen is well nigh perfect.

Etching with oxalic acid is a new method. According to available information, which has been confirmed, it is admittedly a dual purpose reagent. Carbides are first resolved, and by continued etching for several seconds, grain boundaries appear. This behavior places the reagent in the class of nitric acid and others mentioned above. Its successful use depends upon stopping the action before any constituents except carbides are resolved, and this feature appears to be a distinct disadvantage.

In comparison with these other methods, electrolytic etching with the NaCN solution appears to be far superior. It is slow acting, and sensitive to carbides alone for an etching period much in excess of what is required to reveal carbides. It defines carbides sharply, and reveals clearly the minutest traces of precipitation. Even if specimen polishing is slighted somewhat, results are fairly reliable, in sharp contrast with other methods which are valueless under these conditions. It is true that ferrite pools in an annealed carbide-free structure are outlined, and that one or more constituents within the ferrite areas etch dark when precipitated carbides are present, but this is not confusing because ferrite can invariably be recognized for what it is.

4. *Quantitative Measurement of Carbide Precipitation with the NaCN Test*—Although the phenomenon of carbide precipitation has been intensively studied, no thoroughly satisfactory or generally accepted explanation of its nature or of the mechanism of its occurrence has been offered. In a broad sense, carbide precipitation in 18-8 steels is primarily a function of carbon content, and prior treatment (including both hot and cold working). Also, it has been observed that 18-8 is, under some conditions, sensitive ("sensitized") to intergranular corrosion when carbides are precipitated. Moreover, it is usually conceded that 18-8 steels containing high carbon are more susceptible to carbide precipitation than otherwise similar low carbon steels. In consequence, it is customary to adopt precautionary measures in the manufacture and fabrication of these metals looking toward strictly limiting the amount or degree of carbide precipitation, by specifying carbon not over 0.07 or 0.08 per cent, and by carefully governing all operations, and especially welding, to minimize exposure of the metal to temperatures which cause precipitation, or at least to correct the effect of such treatment by subsequent annealing.

Progress in the understanding of carbide precipitation has naturally led to a widespread search for a test which will measure the amount or degree present. This effort has been carried further to the point of attempting to predict or infer susceptibility to intergranular corrosion in service by deliberately imposing controlled carbide precipitation heat treatments upon laboratory specimens and then measuring the amount of carbides precipitated.

The NaCN test has been proposed for these purposes. It has already been determined that the test is a sensitive indicator of car-

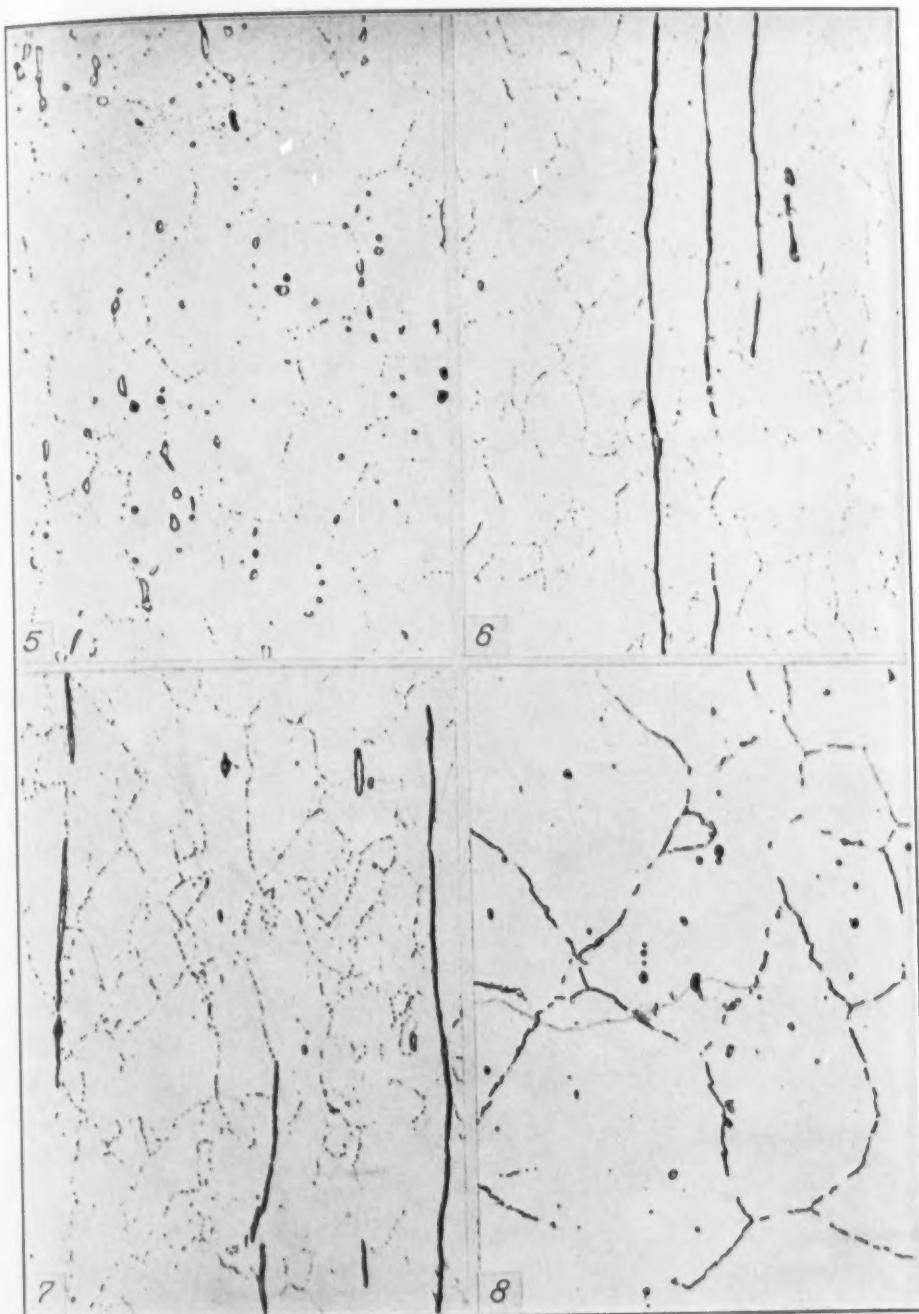


Fig. 5—Annealed and Welded. Area in Parent Metal Adjacent to Fusion Line. Mild Carbide Precipitation Normal to Fabrication Methods. 5 Minute Etch. C 0.05, Cr. 19.3, Ni 8.3.

Fig. 6—Annealed + 1200 Degrees Fahr.—5 Min. C 0.05, Cr 19.1, Ni 8.5. 5 Min. Etch.

Fig. 7—Annealed + 1250 Degrees Fahr.—10 Min. C 0.06, Cr19.3, Ni 8.8. 5 Min. Etch.

Fig. 8—Annealed + 1200 Degrees Fahr.—60 Min. Severe Carbide Precipitation Treatment. C 0.06, Cr 19.2, Ni 8.3. 5 Min. Etch. All Electrolytically Etched in NaCN—6 Volts.  $\times 500$ .

bides. Will it also permit their quantitative measurement? Figs. 5 to 8 illustrate the appearance of annealed specimens which were welded (Fig. 5), or which were heated at 1200-1250 degrees Fahr. (650-675 degrees Cent.) for five, ten and sixty minutes, respectively, and thereby subjected to increasingly severe carbide precipitation treatments.

Undeniably these photographs show that some darkening of the carbides is brought about by greatly prolonging the treatment. Hence, it might seem that the change in appearance could be quantitatively interpreted, but upon close examination it appears there is little significant or clearly definable difference in the structures intermediate between Fig. 5 and Fig. 8. Even the common variable of etching technique may have a pronounced effect, as is illustrated in Figs. 7 and 9, which compare identical specimens etched five and twenty minutes, respectively.

Such results do not encourage the use of the NaCN test for quantitative measurement of the amount or degree of carbide precipitation. This is especially true since a judicious choice of materials and processing methods makes it practical to severely limit the amount of precipitation, and thus unnecessary to evaluate minute increments in the quantities of carbides present: differences between a trace and slightly more than a trace. The test is very sensitive, and does clearly reveal slightest traces of carbide precipitation (Fig. 5), and in a broad sense it also discriminates between mild and severe precipitation (Figs. 5, 8, 11 and 12). However, the severe conditions shown in Figs. 8 and 12 can be avoided and should not occur, unless by sheerest accident. Therefore, to use this test quantitatively it is necessary to evaluate slight variations from the order of magnitude revealed in Figs. 5, 6, 7 and 10, and considering alone such factors influencing the appearance of carbides as prior treatment, and the variables of specimen preparation and etching technique, this micrometer use of the test is obviously impractical.

5. *Effect of Prior Treatment* — It has been generally recognized that prior treatment influencing grain size and hardness has a marked effect upon the distribution of precipitated carbides (Figs. 10 to 14). Usually hot-rolled or cold-worked materials reflect more or less grain refinement or distortion, and these effects tend to cause precipitated carbides to appear globular and discontinuous. The NaCN test has been proposed for distinguishing between these differences in distribution.

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Fig. 9—Annealed + 1250 Degrees Fahr.—10 Min. C 0.06, Cr 19.3, Ni 8.8. 20  
Min. Etch. Exaggeration of Carbide Effect Due to Over Etching.  
Fig. 10—Hot-Rolled + 1250 Degrees Fahr.—10 Min. C 0.06, Cr 19.2, Ni 8.3  
5 Min. Etch.  
Fig. 11—Hot-Rolled + 1250 Degrees Fahr.—5 Min. C. 0.15, Cr 18.1, Ni 8.0  
5 Min. Etch.  
Fig. 12—Hot-Rolled + 1250 Degrees Fahr.—1 Hour. C 0.15, Cr 18.1, Ni 8.0  
5 Min. Etch. Electrolytically Etched in NaCN—6 Volts.  $\times 500$ .

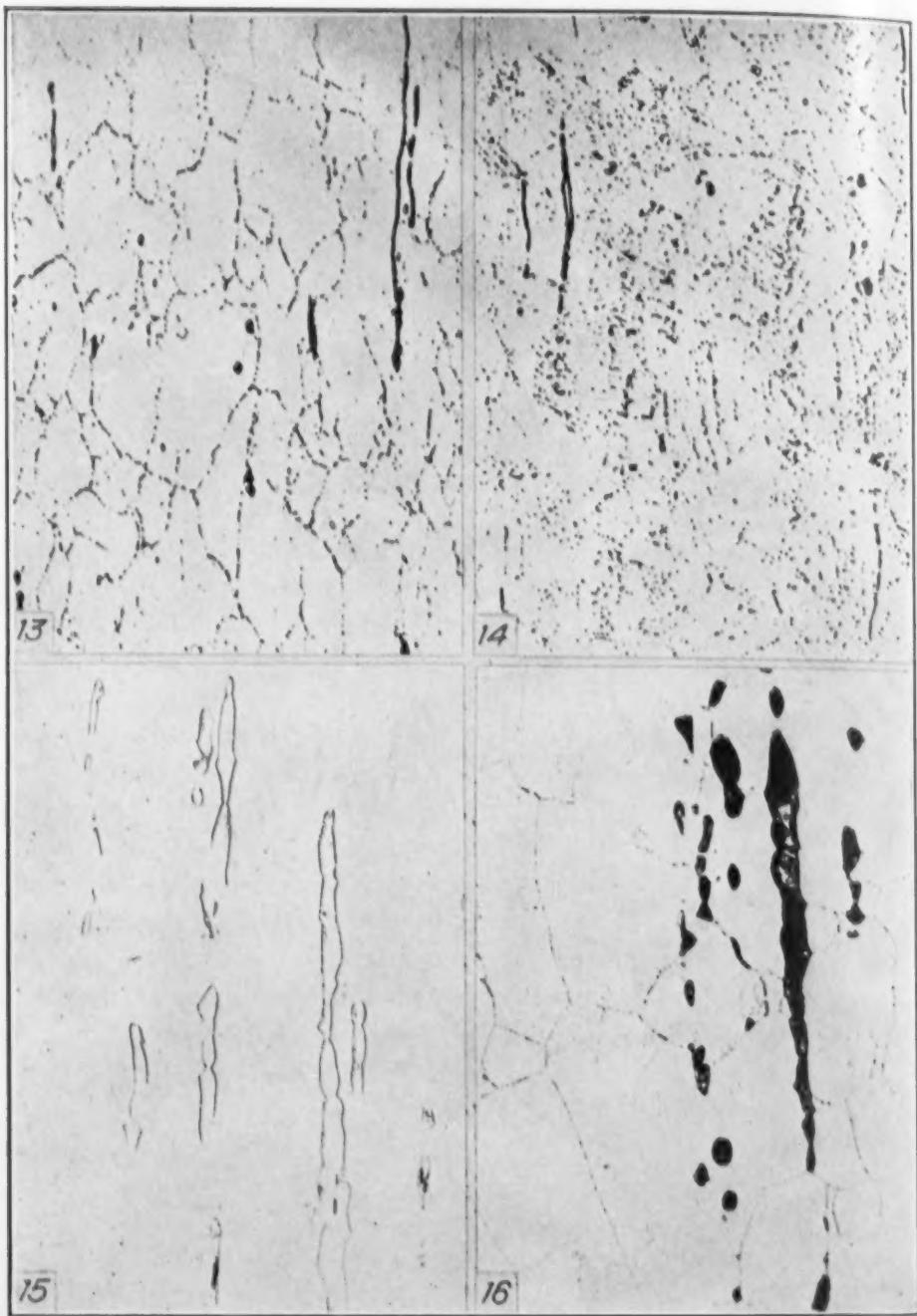


Fig. 13—Annealed + 1250 Degrees Fahr.—10 Min. + Cold Work. Distortion of Carbide Networks by Cold Work. C 0.06, Cr 19.3, Ni 8.8.

Fig. 14—Annealed + Cold Work + 1250 Degrees Fahr.—10 Min. Heterogeneous Dispersion of Carbides Resulting from Precipitation in Strained and Distorted Structure. Analysis same as Fig. 13.

Fig. 15—Annealed. No Carbides, But Ferrite Pools Lightly Outlined. C 0.10, Mn 3.4, Cr 19.6, Ni 8.3.

Fig. 16—Annealed + 1250 Degrees Fahr.—12 Hours. Severe Carbide Precipitation Treatment. Carbides in Boundaries. Also Some Constituent, Probably Carbides, Appears Prominently in Ferrite Pools. Analysis same as Fig. 15. 5 Min. Etch. Electrolytically Etched in NaCN—6 Volts.  $\times 500$ .

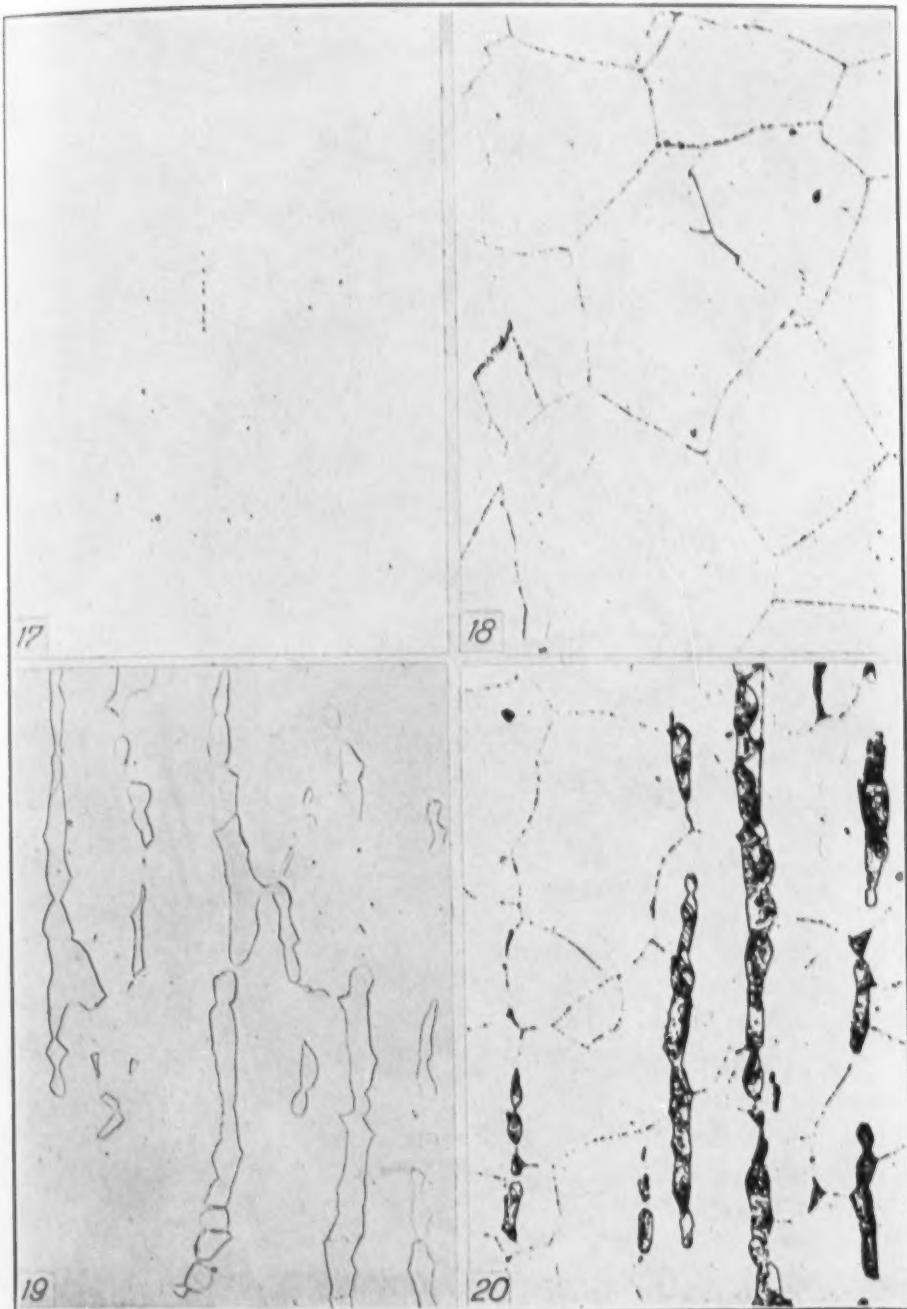


Fig. 17—Annealed.

Fig. 18—Annealed + 1250 Degrees Fahr.—12 Hours. Analysis Figs. 17 and 18—C 0.12, Cr 17.3, Ni 11.2, W 2.6.

Fig. 19—Annealed.

Fig. 20—Annealed + 1200 Degrees Fahr.—24 Hours. Analysis Figs. 19 and 20—C 0.07, Cr 18.8, Ni 9.0, Mo 2.5. Electrolytically Etched in NaCN—6 Volts. 5 Min. Etch.  $\times 500$ .

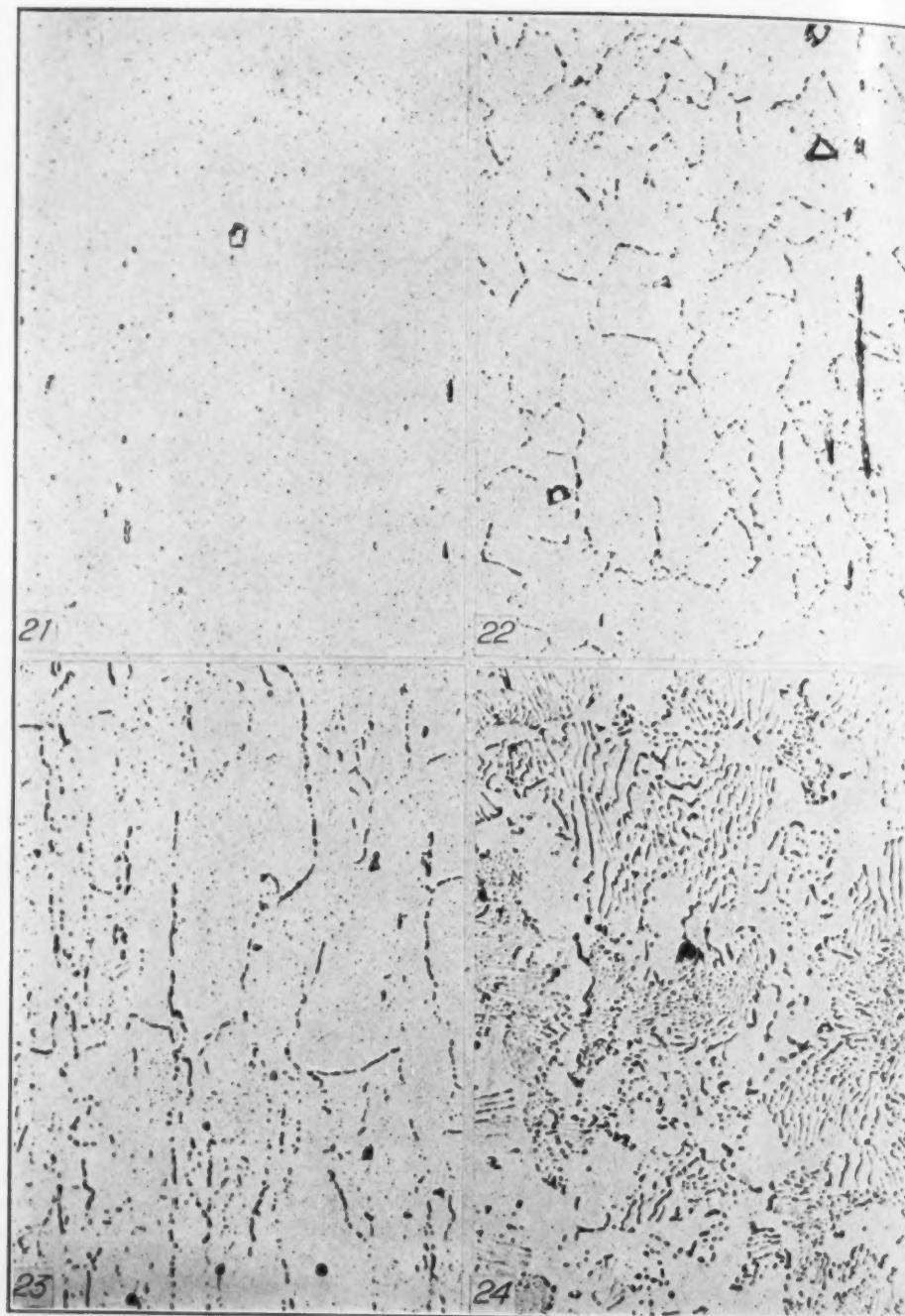


Fig. 21—Annealed.

Fig. 22—Annealed + 1250 Degrees Fahr.—10 Min. Analysis Figs. 21 and 22—C 0.08, Cr 18.0, Ni 9.4, Ti 0.35. 5 Min. Etch.

Fig. 23—Specimen Etched 2 Min. Analysis—C 0.09, Cr 17.75.

Fig. 24—Specimen of 0.52 Per Cent Carbon Steel Treated at 1370 Degrees Fahr.—Slow Cool. Etched 2 Min. All Specimens Electrolytically Etched in NaCN—6 Volts.  $\times 500$ .

Whether globularized carbides, either thoroughly dispersed or in dotted discontinuous networks, are preferable to a continuous network form, however faint, is an open question. It will suffice here to assert that the NaCN test when properly used does differentiate clearly between the extremes of these two forms. Unfortunately, there is a range of conditions wherein one form merges almost imperceptibly into the other, so that it is impossible to define where one ends and the other begins, and hence the NaCN test cannot be expected to determine this end-point with accuracy.

#### TEST PROCEDURE

1. *Preparation of Specimens* — The first step in applying the NaCN test is the proper polishing of specimens. In general, metallographic polishing technique is well understood, but the austenitic stainless steels are peculiarly susceptible to local work hardening, pitting, scratching and flowing of the surface. All such undesired effects as these detract from the consistency and reliability of the test results. Therefore, polishing methods adopted should avoid or minimize these variables, and moreover should be carefully standardized. One satisfactory polishing method is briefly outlined:

Rough polishing by hand to 000 Manning papers used dry.  
Semi-final polishing with levigated (one-half hour) alumina on a 14-inch disk covered with broadcloth, rotating at about 800 revolutions per minute.

Final polishing with alumina levigated two hours, on a 14-inch disk covered with broadcloth, rotating at about 600 revolutions per minute.

*The NaCN Solution* — The analytical grade of NaCN sold by any one of several reliable chemical supply companies has been found satisfactory. The etchant is composed as follows:

NaCN (analytical grade)	10 grams
Distilled water	100 ml.

The solution is used at room temperature.

It is important that the content of chloride impurities be very low. One representative grade of NaCN has been found to contain about 0.02 per cent chlorides, an amount believed insufficient to affect the selectiveness of the etchant. Presence of chlorides causes chloride ion concentration at the anode, a condition which may lead to actual etching of austenite crystal boundaries in the absence of precipitated carbides.

2. *Etching Procedure* — Equipment required is simple, and may

vary in construction or assembly. A satisfactory apparatus is shown in Fig. 25.

The cathode (a) may be a flat piece of platinum attached to a piece of copper wire. The specimen (b) which acts as the anode is so placed that the polished surface is parallel to, and about one inch from, the platinum cathode. Etching is accomplished by making contact with the specimen by means of the stylus (c). The current is supplied by dry cell batteries connected in series.

Current density, and therefore rate of etching action, is governed by size of specimen, distance between anode and cathode, and current potential. A potential of six volts, usually secured by connecting

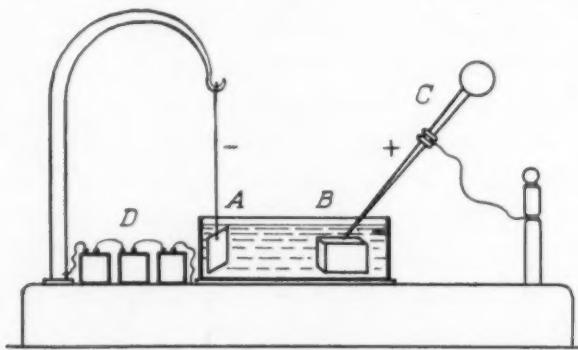


Fig. 25—Diagram of Electrolytic Etching Apparatus.

four standard dry cells in series, is satisfactory. These factors may and do vary over a considerable range, and they regulate the etching time required.

In general, the shortest etching time which yields sharp definition of carbides is to be preferred. At least one large user of 18-8 who employs this test extensively favors a five-minute etch. Although this is often a more drastic treatment than is required for a properly polished specimen containing precipitation carbides, it does not generally cause severe over-etching. On the other hand, if no carbides are revealed in a properly polished specimen after etching for five minutes, it may be safely assumed that none are present.

There is no serious objection to general adoption of these test conditions in the interest of uniformity and standardization, but it is not believed that they are necessarily the optimum conditions, or even that they need be arbitrarily specified.

3. *Examination*—It has been the practice in several laboratories to make routine examination of specimens at  $\times 500$ . This procedure is generally satisfactory, although higher magnification brings

out much interesting and perhaps significant and essential detail.

4. *Mechanism of the Test*—Despite substantial evidence of the reliability and usefulness of the NaCN etch for qualitative tests, it is doubtful if a critical study of it has been made. The chemistry of the etching action is not yet thoroughly understood, nor is the nature of the attack altogether clear. A careful investigation, especially of the structures revealed at high magnification, would prove most welcome. It is to be hoped that this task will be soon undertaken.

In the meantime, a very cursory analysis will have to suffice. Evidently, the oxidizing conditions set up at the anode when etching with this reagent are induced by nascent oxygen formed in the breaking down of hydroxyl ions. In addition, it is probable some cyanate is formed, and chlorine also, if chlorides are present. Carbides are probably attacked by these agents, and presumably the austenitic matrix is maintained stable by the passivating effect of the oxygen.

Reference to Fig. 4 will show that even the low chloride solution does attack austenite under special conditions. This photograph suggests that the metal is being dissolved by a strong oxidizing attack, similar to what is observed in concentrated nitric acid.

#### SUMMARY AND CONCLUSION

The NaCN test has been carefully examined, typical results are recorded, and a safe test procedure has been outlined.

The NaCN solution will not etch the austenite structure of 18-8 steel unless exposure to the solution is prolonged much beyond the time required to etch carbides, if any are present.

When carbides are precipitated, etching for several minutes will reveal them. Overetching, unless inordinately prolonged, does not affect or confuse qualitative results in the slightest.

It is clear that the NaCN solution outlines ferrite pools in the annealed structure, and etches them dark when carbides are precipitated, but this result does not detract from the usefulness of the test, because the appearance of ferrite cannot be mistaken.

In general, this test appears suitable for detecting the presence of precipitated carbides (chromium carbides, tungsten carbides, etc.) in the structures of 18-8 alloys. Its sensitiveness is not affected by presence of the usual addition agents, but it fails to identify separately the carbides of these various added elements.

Because it is reliably selective in its preferential attack of carbides for a much longer etching period than is required to etch them, the NaCN test is deemed superior to all dual purpose reagents for revealing the presence of precipitated carbides. In comparison with Murakami's reagent, the NaCN solution achieves somewhat better definition, more uniform etching, and more reliable results, especially if polishing is less than perfect.

Although the NaCN test may be used to detect the difference between incipient and severe carbide precipitation, the condition of greatest practical importance is the incipient condition incident to welding or to processing of materials. For detecting or evaluating minute differences in the very mild degree of carbide precipitation involved, the NaCN test is not suitable and is not recommended.

The NaCN test will clearly reveal differences in the form or distribution of carbides. However, it cannot be applied satisfactorily to establish the end point where the globular form merges into the continuous network form.

It follows that the only proper uses of the NaCN test which can be approved as yet are for investigational work in studying the phenomenon of carbide precipitation, and for production work to differentiate between materials that are completely, or at least substantially, free of precipitation as contrasted with materials that are definitely sensitized. For these uses it is eminently suited, has proven superior to others, and is much quicker.

In closing the author wishes to express his appreciation to the metallurgical staff of the Rustless Iron and Steel Corp. for their indispensable assistance, and especially to Messrs. S. P. Watkins and E. H. Wyche, who developed the test procedure outlined and conducted the metallographic work upon which the report is based. Other metallurgists prominent in the industry, including Messrs. F. B. Foley, R. P. DeVries, John Brunner and H. E. Passmore, contributed valuable editorial comment and data from their own laboratories, and their assistance is gratefully acknowledged. To the management of the Rustless Iron and Steel Corp. thanks are due for their friendly interest and co-operation in fostering this work.

**Written Discussion:** By Ernest H. Wyche, Rustless Iron and Steel Corp., Baltimore Md.

THE SODIUM CYANIDE CARBIDE ETCH AS  
APPLIED TO THE 18-8 FREE MACHINING STEELS

It has recently been observed that sulphides in the 18-8 free machining

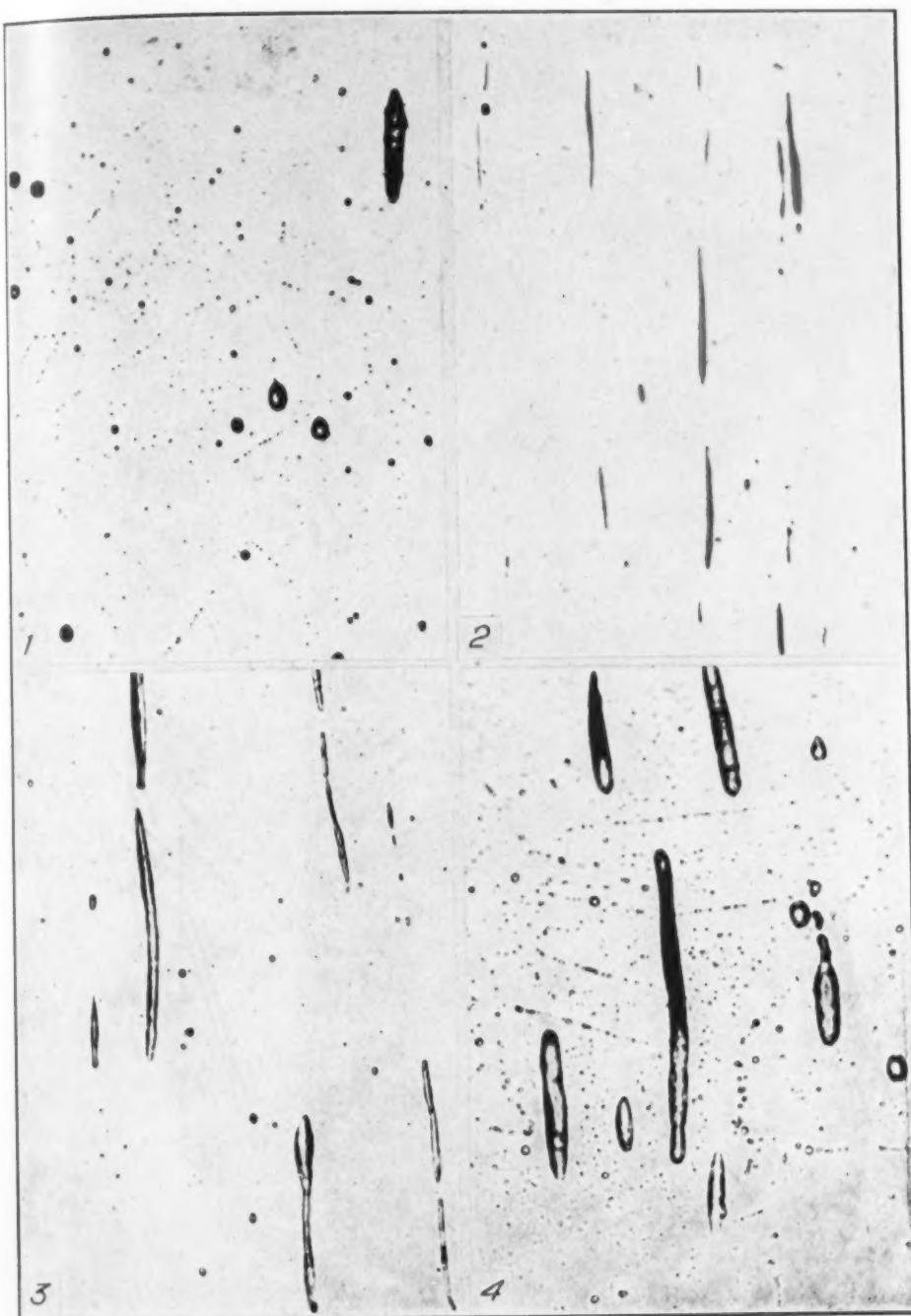


Fig. 1—Annealed Specimen of the Following Analysis Etched Electrolytically for 5 Minutes in NaCN. Six-Volt Current.  $\times 500$ . C 0.08, S 0.27, Cr 18.11, Ni 8.44, Mo 0.36.

Fig. 2—Unetched Specimen.  $\times 500$ . Analysis Same as Fig. 3.

Fig. 3—Etched Specimen. Annealed. 5 Minute Electrolytic NaCN Etch.  $\times 500$ . C 0.07, S 0.22, Cr 18.51, Ni 8.82, Mo 0.41.

Fig. 4—Specimen Same as Fig. 1. 20 Minute Electrolytic NaCN Etch.  $\times 500$ .

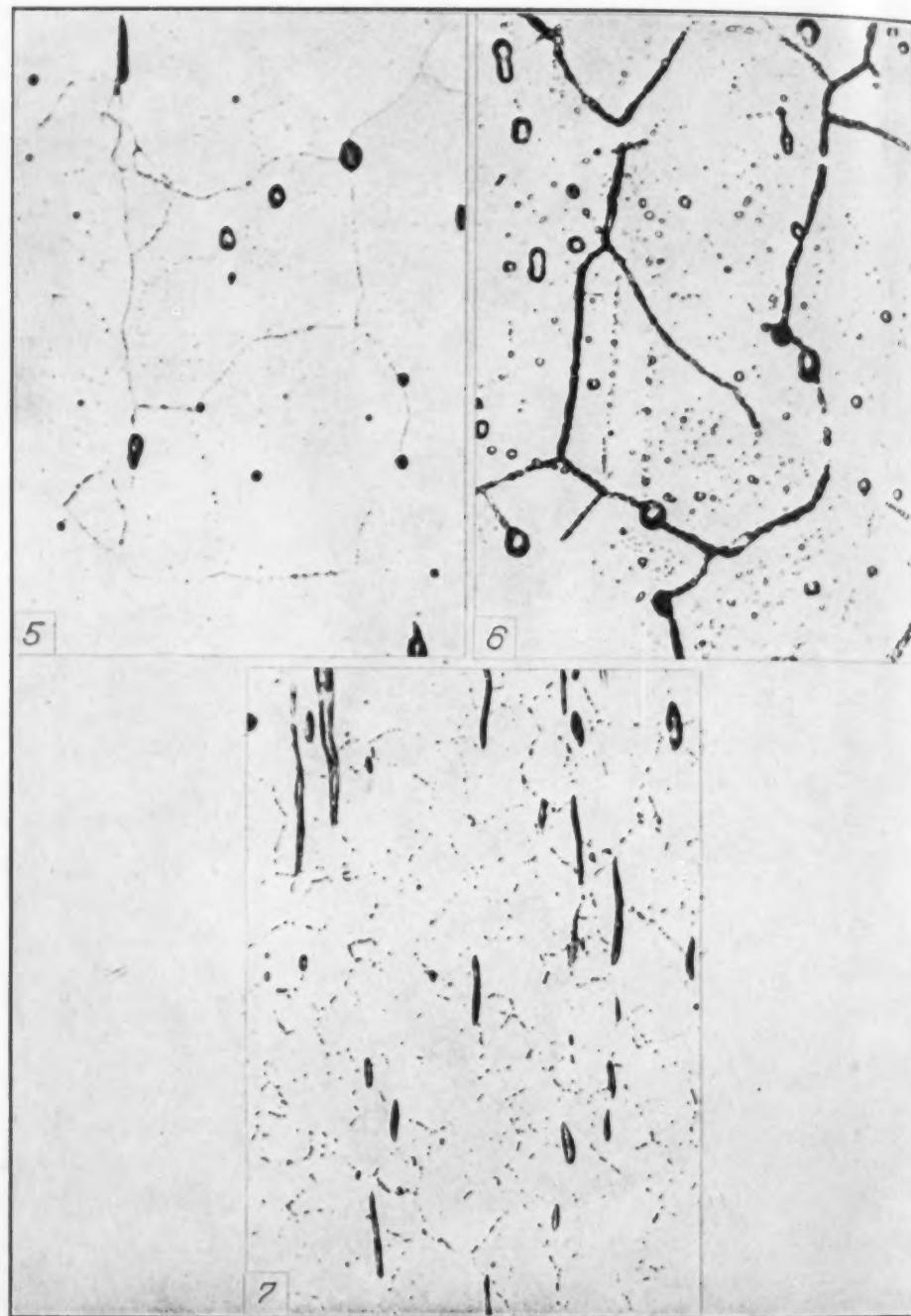


Fig. 5 and Fig. 6—Same Specimen Shown in Figs. 1 and 4. Plus 1250 Degrees Fahr. 10 Minutes. Fig. 5 Electrolytic NaCN Etch for 5 Minutes. Fig. 6 Same Etched 20 Minutes.  $\times 500$ .

Fig. 7—Normal Specimen Having Precipitated Carbides and No Small Sulphides. 5 Minute Electrolytic NaCN Etch. C 0.07, S 0.31, Cr 18.11, Ni 9.08, Mo 0.41.  $\times 500$ .

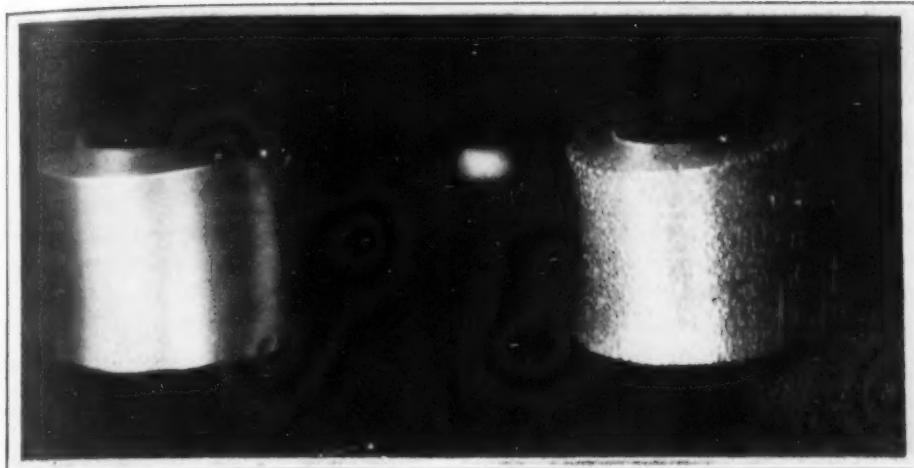


Fig. 8—Copper Sulphate Bend Tests. Left—OK. Right—Bad. Dents Are Due to Jaws of Vise.  $\times 2$ .

grades are sometimes found dispersed in a pattern strikingly similar to lightly precipitated carbides after a micro specimen has been electrolytically etched with NaCN. Fig. 1 is an illustration of this phenomenon found in fully annealed and therefore carbide-free material.

Thus arose the problem of deciding whether a given specimen was actually carbide-free or not. The development of a special etching technique for identifying both components had to be worked out, and below three methods are outlined which have enabled us to arrive at a correct interpretation of results.

The first method for solving doubtful cases was based upon a careful microscopic examination at about  $\times 500$ . Three marked differences were noted in the appearance and orientation of the two constituents, even though both were resolved in about the same etching time. Typical photomicrographs of unetched and etched specimens showing normal sulphide distribution are illustrated in Figs. 2 and 3.

The first difference in appearance was seen by moving the microscopic field slowly in-and-out of focus. Sulphides were found to have a white "core" when etched (Fig. 3), while carbides are known to be solid black when etched. This white appearance is probably due to a reflection of light from the bottom of the hole left by dissolving out a sulphide. It was sometimes necessary to accentuate this difference by over-etching for as long as four or five times the usual amount in order to see the white "cores" of the smallest sulphides. Figs. 4 and 6 illustrate the result of over-etching specimens of Figs. 1 and 5 respectively, and they plainly show the white "cores" of the larger sulphides. Figs. 1 and 4 are carbide-free; Figs. 5 and 6 contain carbides.

A second distinct difference in appearance was noted in the general orientation of small sulphides and precipitated carbides. The sulphides were more often aligned in straight rows of dots and scattered throughout the grains (Fig. 4), while carbides were in curved rows of dots (Fig. 7).

A third difference in appearance was noted in general distribution of sulphides and carbides when taken over large areas. Sulphides of all sizes seem

to be somewhat segregated in bands aligned in the direction of rolling or working, while carbides, when present, are known to be rather uniformly distributed over the entire surface.

The second method of solving doubtful cases was by heat treating a portion of the specimen. It was either annealed to dissolve carbides, or was heated at 1250 degrees Fahr. (675 degrees Cent.) to precipitate carbides, and after etching, was compared with the original. If one did not have sufficient material and did not wish to destroy the previous structural condition, this second method would not be advisable. Fig. 5 illustrates the result of a 1250 degree Fahr. (675 degree Cent.) treatment given the specimen shown in Fig. 1. When over-etched (Fig. 6), the carbides, if continuous, appear in heavy black lines.

The third method for solving doubtful cases was by subjecting a specimen to the familiar Strauss acid copper sulphate test. The results of two such tests are illustrated in Figs. 1, 2, 5, 6 and 8. The structure of the satisfactory bend test pictured on the left in Fig. 8 is shown by Figs. 1 and 2, while the structure of the other bend test, which failed to pass the Strauss test, is illustrated by Figs. 5 and 6. A normal specimen having precipitated carbides and no small sulphides is shown in Fig. 7.

#### CONCLUSION

The fact that the sodium cyanide reagent resolves both carbides and sulphides is no valid reason for discarding this etchant, because the other reagents most commonly used for detecting carbides, namely Murakami's reagent and oxalic acid, also resolve these same constituents.

The results obtained by electrolytically etching 18-8 free machining with sodium cyanide become difficult of interpretation only when the sulphides are finely dispersed. Normally, the specimen appears similar to that illustrated in either Fig. 3 or Fig. 7, which respectively show structures without and with carbides.

Although the writer is not as familiar with 18-8 containing selenium and other free machining grades as with 18-8 containing sulphur, it is his experience that similar dispersions are sometimes encountered in the examination of these other grades, and that these methods also apply for them.

## THE MICROCHARACTER AS A RESEARCH TOOL

BY W. J. CONLEY, W. E. CONLEY, H. J. KING AND L. E. UNGER

### Abstract

The "microcharacter," an instrument which can be used to determine the relative hardness of the microscopic constituents of alloys, is described together with the technique of its operation and interpretation of the results. The fundamental reasons for the adoption of the diamond point as the cutting tool, ground to the shape of the corner of a cube, are stated. Microscopic illustrations are included to show the range of hardness determinations possible and tables showing the conversion from width of cut in microns to microhardness. A table is also given of hardness determinations for several metals and microconstituents of alloys as found by the authors. Finally some examples show the practical possibilities of the instrument for the recognition of structures, the determination of machinability of steel and the study of the case on case-hardened steels.

SEVERAL years ago the authors, through contact with some practical bearing problems, found it necessary to know more about the function of the various constituents of bearing alloys. Since performance seemed to bear a relation to the relative hardness of the microscopic components of the materials of the bearings, search was made to find a means of evaluating this hardness. It was clear that the common practical methods for the determination were not applicable to this problem.<sup>1</sup> As a result of a diligent search attention was drawn to the "microcharacter,"<sup>2</sup> and this instrument seemed to have the required requisites. After some preliminary investigation, the device itself seemed to offer a very fascinating field for study and consequently, considerable research has been done by the authors on the technique of this apparatus.

Inasmuch as the "microcharacter" was not a universally known instrument and is used only to a limited extent, and since it seemed

<sup>1</sup>An excellent summary of the work to date is given in "The Hardness of Metals and its Measurement," by Hugh O'Neil.

<sup>2</sup>C. H. Bierbaum, "The Microcharacter," TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 1009.

Of the authors, W. J. Conley is professor of engineering, and the others graduate students of the University of Rochester, Rochester, N. Y., Manuscript received June 22, 1936.

to offer possibilities for the attack of many problems in research, it was felt that a description of the instrument and some of its applications might be of interest to a considerable number of research workers.

The "microcharacter" was developed by C. H. Bierbaum<sup>3</sup> who considered several shapes in the design of a proper cutting edge. Mr. Bierbaum was governed in his choice by the following:

1. The formations to be tested were of microscopic size and, consequently any hardness measurements had to be made on very minute areas.
2. The cutting edge had to be sufficiently sharp to produce a clear cut on exceedingly hard as well as soft material.
3. In order to obtain absolute values and for comparative results the cutting edge had to be ground accurately to definite specifications which afford exact duplication.
4. The shape had to be such that at all times the vertical pressure exerted upon the material tested had to be greater than the horizontal cutting force, also, that the depth of indentation could not be increased by removing the horizontal pull upon the cutting edge.

A cutting point in the shape of a solid right angle (Fig. 1) or the corner of an imaginary cube was selected as best fulfilling the

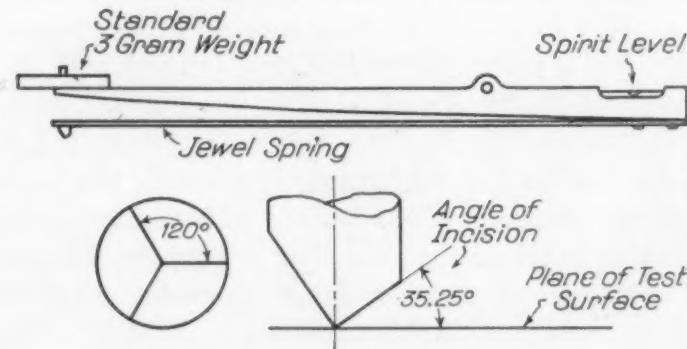


Fig. 1—Showing Shape of Cutting Point and Also the Method of Elastically Mounting.

above conditions. This point was mounted with its axis vertical and with one corner constituting the cutting edge. The intersection of the two points makes an angle of 35.246 degrees with the test surface. This constitutes the angle of incision. Since the instrument had to

<sup>3</sup>Vice-president and consulting engineer, Lumen Bearing Co., Buffalo, N. Y.

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be sensitive to sharp changes in hardness, the cutting point had to be mounted elastically (Fig. 1).

It seems obvious that the diamond would be first choice to fulfill the above specifications, but due to the difficulty in grinding, an artificial sapphire was first used. Finally, a lapidarian<sup>4</sup> was found who was able to grind a diamond to the corner of a square, so that the point appeared sharp at a magnification of 2000 diameters. At this magnification the three facets were true plane surfaces, their intersections were sharp straight lines and at precise right angles.

#### DESCRIPTION OF INSTRUMENT

The photograph (Fig. 2) shows a complete "microcharacter" constructed for mounting either on a stand or on a microscope stage. The diamond is mounted at the end of a tapered steel spring, the op-

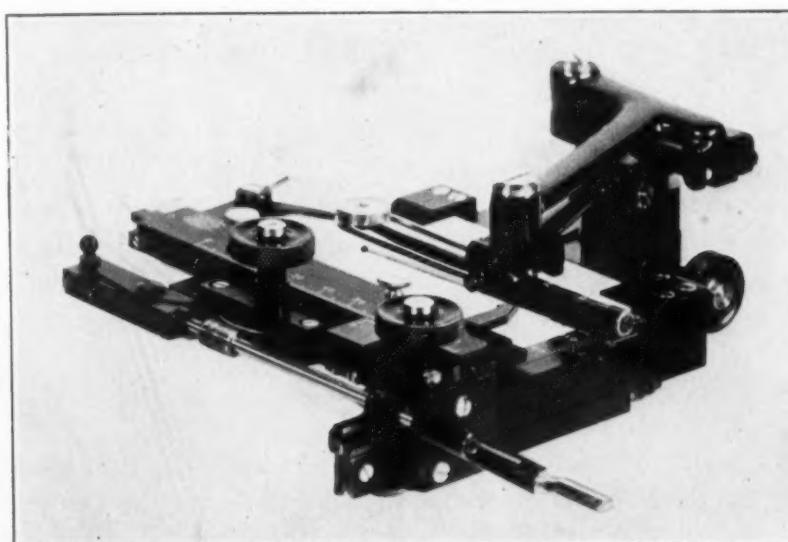


Fig. 2—Photograph of Complete Microcharacter for Mounting on Stand or Microscope.

posite end of which is securely fastened to the balanced arm shown diagrammatically on Fig. 1. A spirit level is provided at one end to insure that the axis of the diamond will be normal to the test surface and that the full load of the weight will be applied to the cutting point. This balanced arm is suspended on sapphire bearings by means of a second bracket which may be raised or lowered by a

<sup>4</sup>F. F. Gilmore, Boston, Mass.

rack and pinion. For convenience the suspension bracket may be swung back out of the way when inspecting or removing test specimens.

The specimen, properly polished and lightly etched, is mounted in plasticine on a glass slide which is then clamped onto the mechanical stage similar to that used on an ordinary microscope. The specimen is drawn under the diamond point by a micrometer feed actuated by hand or a power driven worm and worm wheel which is attached to the longitudinal displacement of the mechanical stage. During cutting the diamond point is lubricated with a superfine watch oil. After completing the cut, the piece is removed and swabbed with xylol to remove the lubricant. The specimen may then be taken to the microscope equipped with a Filar micrometer which has been calibrated, allowing measurements of cut widths to  $\frac{1}{10}$  of a micron. It is obvious that it is necessary to have the highest grade of microscopical equipment in order to obtain satisfactory results. The authors have found that optical equipment giving magnifications of 500, 800, 1200, 2600 and 4400 diameters is sufficient for the range of readings which they encountered. These readings were made in lead as the softest and in cementite in white cast iron which was the hardest material encountered.

The microhardness scale, devised expressly to interpret the results obtained with the "microcharacter" has been retained as a standard. This is derived by using the reciprocal of the cut width in microns squared, multiplied by 10,000. Thus, the expression for

microhardness reads,  $K = \frac{10,000}{\lambda^2}$  where K is microhardness,  $\lambda$

is the cut width in microns and 10,000 is an arbitrary number used to avoid fractional hardness values. Table I shows the method used by the authors for obtaining microhardness directly from Filar micrometer readings for their apparatus only. It must be remembered at all times that this is a logarithmic scale (Fig. 3) and (Table II), consequently greater uniformity of hardness will be obtained in the range depicting softer materials. For example:

Width of Cut in Microns	Microhardness
(a) { 20 { 19.5	25 26.3
(b) { 1.5 { 1.4	4440 5102

Let the first group (a) represent two readings of cut width and the

Table I  
Microhardness Numbers from Filar Micrometer Reading

Turns	K°	μ	Turns	K	μ	Turns	K	μ
10.0	75.6	11.5	3.2	739.0	3.7	2.34	1381	2.7
9.9	77.2	11.4	3.1	787.0	3.6	2.33	1393	2.7
9.8	78.7	11.3	3.0	840.0	3.5	2.32	1404	2.7
9.7	80.4	11.1	2.99	846	3.4	2.31	1417	2.7
9.6	82.0	11.0	2.98	852	3.4	2.30	1430	2.6
9.5	83.8	10.9	2.97	857	3.4	2.29	1442	2.6
9.4	85.5	10.8	2.96	863	3.4	2.28	1454	2.6
9.3	87.4	10.7	2.95	869	3.4	2.27	1467	2.6
9.2	89.4	10.6	2.94	875	3.4	2.26	1480	2.6
9.1	91.3	10.5	2.93	881	3.4	2.25	1494	2.6
9.0	93.4	10.3	2.92	887	3.4	2.24	1507	2.6
8.9	95.4	10.2	2.91	893	3.3	2.23	1521	2.6
8.8	97.7	10.1	2.90	899	3.3	2.22	1534	2.5
8.7	100.0	10.0	2.89	905	3.3	2.21	1548	2.5
8.6	102.2	9.9	2.88	912	3.3	2.20	1563	2.5
8.5	104.7	9.8	2.87	918	3.3	2.19	1577	2.5
8.4	107.2	9.7	2.86	925	3.3	2.18	1591	2.5
8.3	109.8	9.5	2.85	931	3.3	2.17	1606	2.5
8.2	112.5	9.4	2.84	938	3.3	2.16	1621	2.5
8.1	115.2	9.3	2.83	944	3.3	2.15	1636	2.5
8.0	118.2	9.2	2.82	951	3.2	2.14	1651	2.5
7.9	121.2	9.1	2.81	958	3.2	2.13	1667	2.4
7.8	124.3	9.0	2.80	964	3.2	2.12	1683	2.4
7.7	127.6	8.9	2.79	972	3.2	2.11	1699	2.4
7.6	130.9	8.7	2.78	979	3.2	2.10	1714	2.4
7.5	134.4	8.6	2.77	985	3.2	2.09	1731	2.4
7.4	138.1	8.5	2.76	992	3.2	2.08	1747	2.4
7.3	141.9	8.4	2.75	1000	3.2	2.07	1765	2.4
7.2	145.9	8.3	2.74	1007	3.2	2.06	1782	2.4
7.1	150.0	8.2	2.73	1014	3.1	2.05	1800	2.4
7.0	154.3	8.1	2.72	1022	3.1	2.04	1817	2.3
6.9	158.9	7.9	2.71	1030	3.1	2.03	1835	2.3
6.8	163.6	7.8	2.70	1037	3.1	2.02	1853	2.3
6.7	168.5	7.7	2.69	1045	3.1	2.01	1872	2.3
6.6	173.6	7.6	2.68	1053	3.1	2.00	1890	2.3
6.5	179.0	7.5	2.67	1060	3.1	1.99	1909	2.3
6.4	184.6	7.4	2.66	1069	3.1	1.98	1929	2.3
6.3	190.5	7.2	2.65	1077	3.1	1.97	1948	2.3
6.2	196.7	7.1	2.64	1085	3.0	1.96	1969	2.2
6.1	203.3	7.0	2.63	1093	3.0	1.95	1988	2.2
6.0	210.1	6.9	2.62	1101	3.0	1.94	2009	2.2
5.9	217.2	6.8	2.61	1111	3.0	1.93	2030	2.2
5.8	224.8	6.7	2.60	1119	3.0	1.92	2051	2.2
5.7	232.9	6.6	2.59	1127	3.0	1.91	2072	2.2
5.6	241.2	6.4	2.58	1136	3.0	1.90	2094	2.2
5.5	250.0	6.3	2.57	1144	3.0	1.89	2117	2.2
5.4	259.4	6.2	2.56	1153	2.9	1.88	2144	2.2
5.3	269.1	6.1	2.55	1163	2.9	1.87	2167	2.1
5.2	279.6	6.0	2.54	1172	2.9	1.86	2186	2.1
5.1	290.7	5.9	2.53	1181	2.9	1.85	2210	2.1
5.0	302.5	5.8	2.52	1190	2.9	1.84	2235	2.1
4.9	315.0	5.6	2.51	1200	2.9	1.83	2257	2.1
4.8	328.2	5.5	2.50	1210	2.9	1.82	2283	2.1
4.7	342.0	5.4	2.49	1220	2.9	1.81	2307	2.1
4.6	357.0	5.3	2.48	1230	2.8	1.80	2334	2.1
4.5	373.0	5.2	2.47	1239	2.8	1.79	2360	2.1
4.4	391.0	5.1	2.46	1249	2.8	1.78	2387	2.1
4.3	409.0	4.9	2.45	1259	2.8	1.77	2414	2.0
4.2	428.0	4.8	2.44	1270	2.8	1.76	2441	2.0
4.1	449.0	4.7	2.43	1280	2.8	1.75	2469	2.0
4.0	473.0	4.6	2.42	1291	2.8	1.74	2498	2.0
3.9	498.0	4.5	2.41	1302	2.8	1.73	2526	2.0
3.8	524.0	4.4	2.40	1312	2.8	1.72	2557	2.0
3.7	552.0	4.3	2.39	1324	2.7	1.71	2586	2.0
3.6	584.0	4.1	2.38	1335	2.7	1.70	2614	2.0
3.5	617.5	4.0	2.37	1346	2.7	1.69	2648	1.9
3.4	654.0	3.9	2.36	1358	2.7	1.68	2679	1.9
3.3	694.0	3.8	2.35	1369	2.7	1.67	2711	1.9
3.2	739.0	3.7	2.34	1381	2.7	1.66	2744	1.9

Table I (Continued)

Turns	K	$\mu$	Turns	K	$\mu$	Turns	K	$\mu$
1.66	2744	1.9	1.44	3647	1.7	1.22	5081	1.4
1.65	2778	1.9	1.43	3698	1.6	1.21	5164	1.4
1.64	2811	1.9	1.42	3749	1.6	1.20	5252	1.4
1.63	2846	1.9	1.41	3801	1.6	1.19	5341	1.4
1.62	2881	1.9	1.40	3858	1.6	1.18	5432	1.4
1.61	2917	1.9	1.39	3913	1.6	1.17	5523	1.3
1.60	2953	1.8	1.38	3969	1.6	1.16	5618	1.3
1.59	2991	1.8	1.37	4028	1.6	1.15	5718	1.3
1.58	3029	1.8	1.36	4088	1.6	1.14	5817	1.3
1.57	3067	1.8	1.35	4134	1.6	1.13	5922	1.3
1.56	3108	1.8	1.34	4211	1.5	1.12	6028	1.3
1.55	3147	1.8	1.33	4275	1.5	1.11	6137	1.3
1.54	3189	1.8	1.32	4340	1.5	1.10	6250	1.3
1.53	3230	1.8	1.31	4406	1.5	1.09	6363	1.2
1.52	3273	1.8	1.30	4474	1.5	1.08	6481	1.2
1.51	3316	1.7	1.29	4544	1.5	1.07	6605	1.2
1.50	3361	1.7	1.28	4614	1.5	1.06	6729	1.2
1.49	3406	1.7	1.27	4688	1.5	1.05	6859	1.2
1.48	3452	1.7	1.26	4762	1.5	1.04	6993	1.2
1.47	3500	1.7	1.25	4839	1.4	1.03	7128	1.2
1.46	3547	1.7	1.24	4918	1.4	1.02	7267	1.2
1.45	3596	1.7	1.23	4999	1.4	1.01	7413	1.2
1.44	3647	1.7	1.22	5081	1.4	1.00	7564	1.2

Microscope—B &amp; L FSM with Binocular Eyepiece Adapter.

Objective—B &amp; L 2 mm Achromatic.

Filar Micrometer—Spencer 0.2 mm per turn.

Stage Micrometer—(Used in Calibration) Leitz 0.01 mm.

10,000

$$K = \frac{10,000}{(1.15 \times n)^2}$$

Table II  
Microhardness Numbers—Standard 3-Gram Weight $K = \lambda^{-2} 10^4 =$  Microhardness $\lambda =$  Width of Microcut in Terms of  $\mu$ 

$\mu$	K	$\mu$	K	$\mu$	K	$\mu$	K
50.0	4.0	13.0	59.2	8.6	135	3.6	772
47.5	4.4	12.8	61.0	8.4	142	3.5	816
45.0	4.9	12.6	63.0	8.2	149	3.4	865
42.5	5.5	12.4	65.0	8.0	156	3.3	918
40.0	6.3	12.2	67.2	7.8	164	3.2	977
37.5	7.1	12.0	69.5	7.6	173	3.1	1041
35.0	8.2	11.8	71.8	7.4	183	3.0	1111
32.5	9.5	11.6	74.3	7.2	193	2.9	1189
30.0	11.1	11.4	76.9	7.0	204	2.8	1276
28.0	12.8	11.2	79.7	6.8	216	2.7	1372
26.0	14.8	11.0	82.6	6.6	230	2.6	1479
24.0	17.4	10.8	85.8	6.4	244	2.5	1600
22.0	20.7	10.6	89.0	6.2	260	2.4	1736
20.0	25.0	10.4	92.5	6.0	278	2.3	1891
19.5	26.3	10.2	96.2	5.8	297	2.2	2066
19.0	27.7	10.0	100	5.6	319	2.1	2268
18.5	29.2	9.9	102	5.4	343	2.0	2500
18.0	30.9	9.8	104	5.2	370	1.9	2770
17.5	32.7	9.7	106	5.0	400	1.8	3087
17.0	34.6	9.6	109	4.8	434	1.7	3460
16.5	36.7	9.5	111	4.6	473	1.6	3906
16.0	39.1	9.4	113	4.4	517	1.5	4444
15.5	41.6	9.3	116	4.2	567	1.4	5102
15.0	44.4	9.2	118	4.0	625	1.3	5917
14.5	47.6	9.1	121	3.9	657	1.2	6944
14.0	51.0	9.0	123	3.8	692	1.1	8264
13.5	54.8	8.8	129	3.7	730	1.0	10000

corresponding microhardness in a soft material and the second group (b) the same for a hard substance.

It is seen that a difference of 0.5 of a micron in case (a) causes 5.2 per cent change in the microhardness while in case (b) a difference of 0.1 of a micron is equivalent to a change of 14.9 per cent. With the best optical equipment, measurements to one micron may be made conveniently, but optical calibration with a standard stage

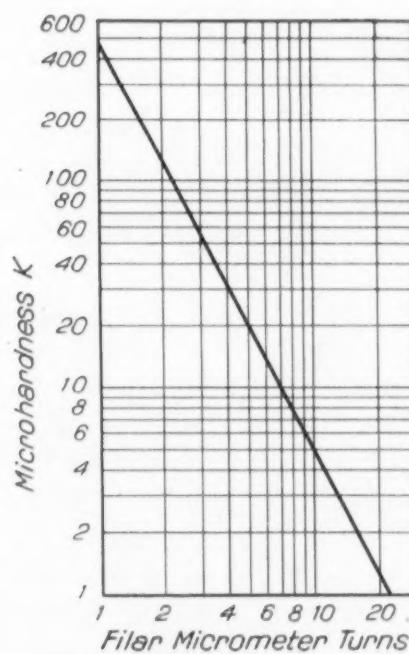


Fig. 3—Logarithmic Scale for Determining Hardness Readings.

micrometer graduated in hundreds of millimeters and the practical limit of magnification as well as the quality of Filar micrometers, make measurements to fractions of a micron doubtful.

The characteristics of the microcut vary in different materials depending upon such factors as ductility and plasticity. The diagram (Fig. 4) shows the cross section of a typical microcut as interpreted by C. H. Bierbaum, while Figs. 5 and 6 show photomicrographs of an actual cut top view and end view. This cut was made by H. J. King in a pure grade of commercial tin, the surface having been prepared by placing the sides of two small blocks of the material together to form one block. The sides were extremely flat so that the edges coincided. This resultant surface was polished and cut at right angles to the mating edges. The blocks were then separated

so that the end of the cut could be observed and photographed. The similarity to Mr. Bierbaum's interpreted cut is extremely striking, so that these photographs are helpful in explaining how to make the readings.

Referring to Fig. 4, all the material displaced by the diamond may be considered pushed out and above and represented by the

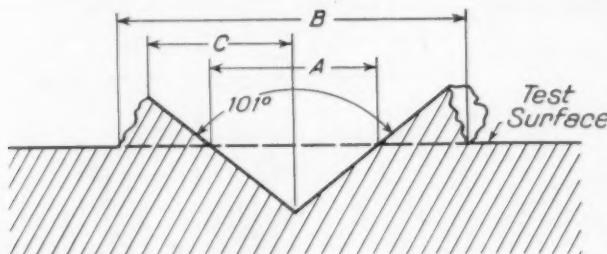
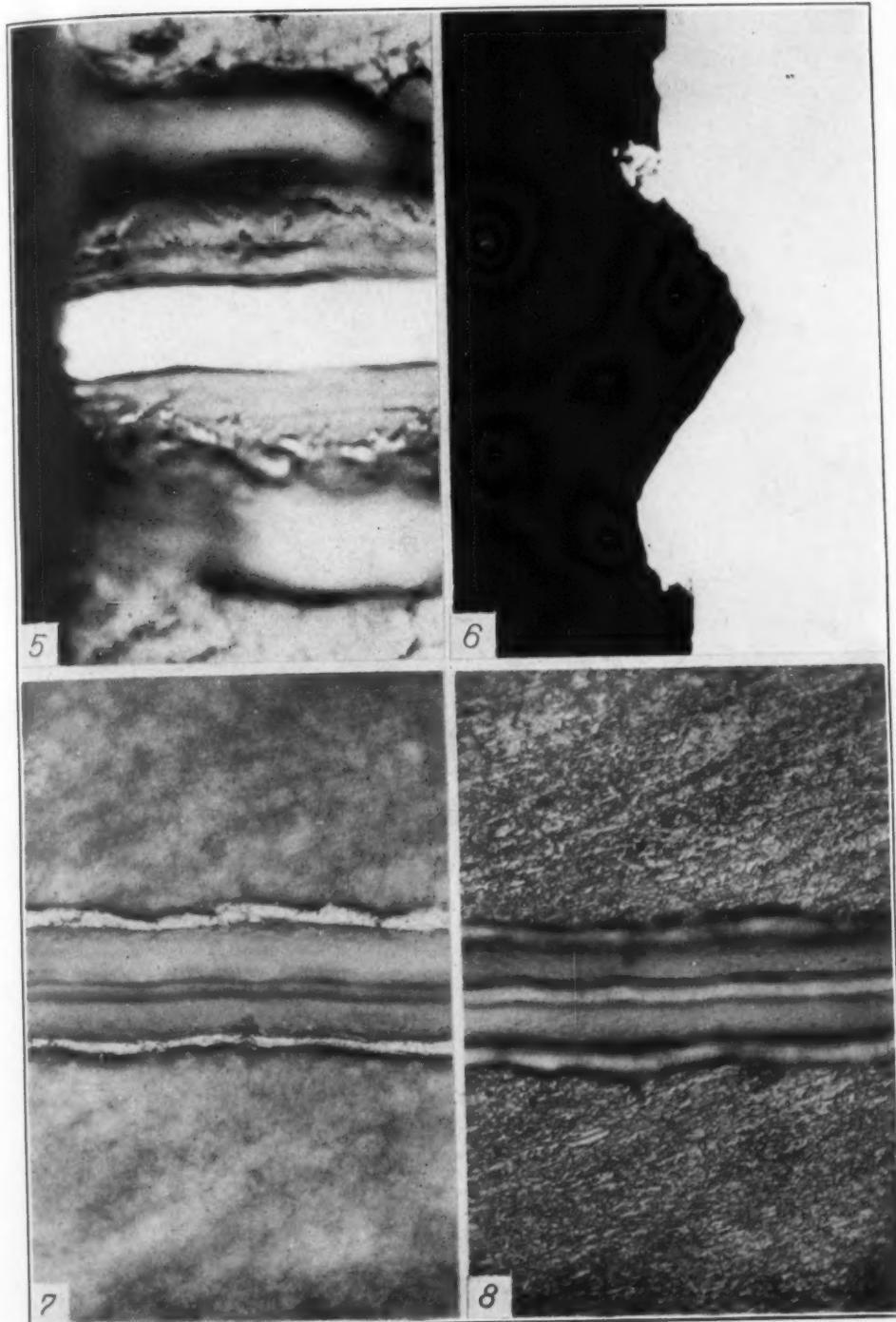


Fig. 4—Diagram Showing Cross Section of a Typical Microcut.

two areas above the test surface. The dimension A seems to be the ideal width to measure, but due to the optical impossibility, it has been found necessary to measure the entire width B of the disturbed material. This undoubtedly leads to error because of the formation of a burr such as shown at the right side of the diagram. The character of this burr has been found to vary in the different materials tested. In many cases the material is displaced outward in such a manner that the dimension C marks a sharp ridge beyond and below which the material slopes to the tested surface. This condition can be better understood by examination of Figs. 7 and 8 or by the actual study of a microcut under the microscope. In other cases the displaced material seems to be entirely burr as shown in Fig. 9. A short break in the burr is shown and, with the exception of a slight ridge, the unaffected test surface adjacent to the cut. Figs. 7 and 8 compare the photomicrograph of a cut in tin taken in focus on the test surface and focused on the ridge rather than this surface. It is recommended in reading the cut width that the microscope be focused on the test surface disregarding the cut and the reading made across the disturbed material where the absence of burr is certain. The appearance of the cut may be improved as regards burr by lightly rubbing with a substance such as the pith from the elder stalk, the pith being saturated with a solution of tin oxide or alumina.

There seems to be no specific linear relation between microhardness and the other common scales of hardness for metals such



Figs. 5 and 6—Photomicrograph of Microcut in Pure Commercial Tin. Fig. 5 Shows the Surface of the Metal with the Microcut.  $\times 1570$ . Fig. 6 Shows the Cross Section of the Metal Through the Microcut.  $\times 1570$ .

Figs. 7 and 8—Photomicrographs of a Microcut in Pure Commercial Tin. Fig. 7 Taken in Focus on Surface of the Metal.  $\times 500$ . Fig. 8 Taken in Focus on the Ridge of the Cut and not the Surface of the Metal.  $\times 500$ .

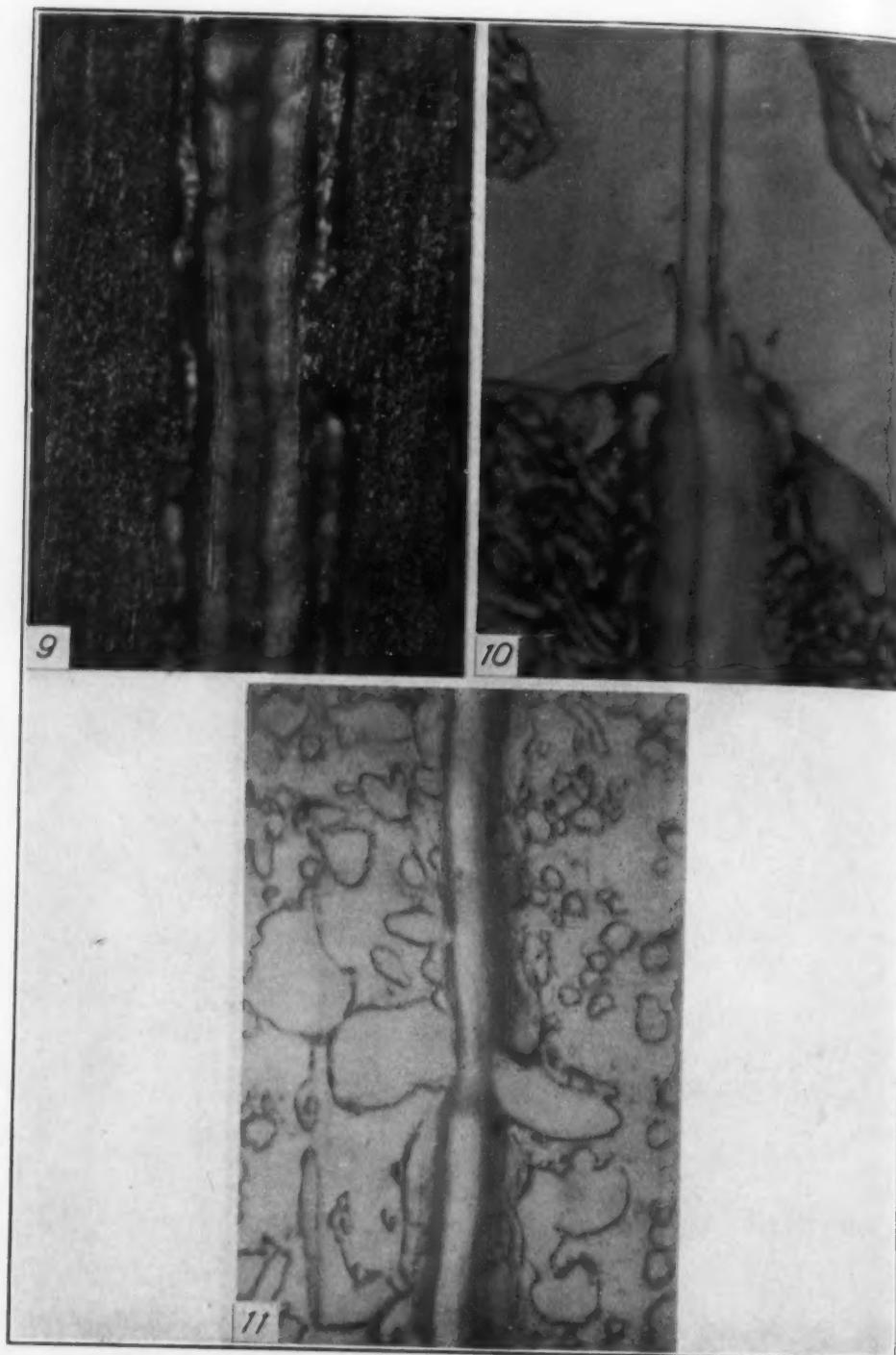


Fig. 9—Photomicrograph of a Microcut in Lead. The Displaced Material Seems to be Entirely Burr. Hardness of 5.  $\times 500$ .

Fig. 10—Photomicrograph of a Microcut in White Cast Iron.  $\times 3000$ .

Fig. 11—Photomicrograph of a Microcut in a 1 Per Cent Carbon Spheroidized Steel Specimen.  $\times 2200$ .

Table III

Material	Brinell Number	Rockwell Number	Martens Number	Microhardness Bierbaum <sup>1</sup> Authors <sup>2</sup>	O'Neill Test	Mohs Scale
Lead	4	..	16.8	7.0 <sup>1</sup>	9.6	1.5
Tin	5	..	26.0	12.2 <sup>2</sup>	24	2
Magnesium (999)	30	..	..	30 <sup>1</sup>	..	2.5
Palladium	45	..	..	108 <sup>2</sup>	..	4
Copper	49	..	40	74-115 <sup>2</sup>	94	3
Armco Iron	80	B 20	44	240 <sup>2</sup>	98	4
Nickel	100	B 60	55.7	244 <sup>1</sup>	..	4
Carburized Steel	720	C 65	208	2950 <sup>1</sup>	..	8
Nitrided Steel	750?	C 67	..	2950 <sup>1</sup>	..	8.5
Cementite	..	..	..	5620 <sup>2</sup>	..	..

as the Rockwell and Brinell scales. Table III has been prepared from various sources to illustrate this. However, Dr. Harold C. Hodge<sup>5</sup> and J. Harold McKay<sup>6</sup> have made a study of the microhardness of minerals constituting the Mohs scale. Table IV is taken from a paper which these authors published<sup>7</sup> in 1934. The Mohs scale is probably the oldest systematic scale of hardness and is now extensively used by mineralogists. This table shows the rather unequal spread of hardness of the key minerals, since there is a greater spread between 7 and 8 than between 6 and 7. The spread between 1 and 6 is small as compared to that between 6 and 7.

Table V shows some of the results obtained by the authors which were found convenient for reference in recognizing the constituents in the alloys studied and for evaluating the aggregate hardness. These results are the average of a great many readings and check closely with readings made by C. H. Bierbaum and Harold McKay using a different instrument.

Table IV

Material	Mohs Scale	Range of Microhardness	Average by H. C. Hodge <sup>1</sup> J. H. McKay <sup>2</sup>
Talc	1	0.8-21.5	1
Selenite	2	10.2-56.6	11
Calcite	3	126-135	129
Fluorite	4	138-145	143
Apatite	5	870-1740	577
Orthoclase	6	2100-2500	975
Quartz	7	2066-3906	2700
Topaz	8	2770-4440	3420
Corundum	9	3906-8264	5300

<sup>1</sup>H. C. Hodge, Senior Dental Fellow, Medical School, University of Rochester.

<sup>2</sup>J. H. McKay, Metallurgist, Lumen Bearing Co., Buffalo, N. Y.

<sup>5</sup>Senior Dental Fellow, Medical School, University of Rochester.

<sup>6</sup>Metallurgist, Lumen Bearing Co., Buffalo, N. Y.

<sup>7</sup>American Mineralogist, Vol. 19, No. 4, April, 1934.

Table V

Material	Width of Microcut, Average in Microns	Microhardness
Lead (Bearium) . . . . .	44.8	5
Tin (Bearium) . . . . .	28.7	12.2
Copper (Bearium) . . . . .	11.6	74
Arco Iron . . . . .	6.5	241
Swedish Iron . . . . .	6.2	257
Ferrite (0.2 per cent Carbon Steel) . . . . .	5.8	297
Ferrite (White Cast Iron, Annealed 4 hours at 1750 degrees Fahr.) . . . . .	5.6	320
Ferrite (Same, for 16 hours) . . . . .	5.4	346
Ferrite (Malleable Iron) . . . . .	4.7	447
Pearlite (White Cast Iron) . . . . .	4.8	427
Pearlite (0.8 per cent Carbon Steel) . . . . .	4.1	600
Pearlite (0.2 per cent Carbon Steel) . . . . .	4.1	600
Pearlite (White Cast Iron, Annealed 16 hours at 1750 degrees Fahr.) . . . . .	3.2	960
Eutectoid Bronze, Annealed . . . . .	4.3	550
Eutectoid Bronze, As Cast . . . . .	4.5-3.1	498-1000
Alpha Bronze* . . . . .	6.6	225
Beta Bronze . . . . .	5.6	315
Gamma Bronze . . . . .	4.7	450
Delta Bronze* . . . . .	3.7	740
Epsilon Bronze* . . . . .	3.9	650
Beta Prime Bronze . . . . .	4.6	473

\*Annealed for 48 hours at 500 degrees Cent.

Figs. 11 and 12 show how well the "microcharacter" accomplishes the functions in the beginning of this paper. Fig. 10 is a photomicrograph at 3000 diameters of a cut in white cast iron. This shows the cut proceeding from a relatively soft material (pearlite) microhardness of 427 to an extremely hard material (cementite) with a microhardness of 5600. It is seen that the cut width can be easily measured in the hard cementite. A lower magnification would give better results for the cut reading in the pearlite, but it can be accurately read as shown. Fig. 11 shows a cut in a 1 per cent spheroidized carbon steel at a magnification of 2200 diameters. The cut crosses a particle of cementite which has not been disturbed or torn from the soft matrix, thus showing that the hardness measurement can be made on small inclusions.

Some definite examples are included which point out the possible uses of the "microcharacter" as an aid in research. In the microscopic study of the copper-tin equilibrium diagram by means of microscopic examinations of various alloys in the series, there was often doubt as to the constituent present. This was true in the case of alloys having composition varying within close limits on either side of a boundary line between two fields. By making cuts on samples which were definitely known, the values of microhardness thus found were used to recognize the structures in the specimens which were less easy to distinguish visually.

In the microscopic investigation of leaded bronzes it was noticed that the structure of the lead in different commercial alloys seemed to vary considerably. The appearance, in some cases, seemed to suggest a lead-tin eutectic. Cuts were made on the matrix of these bronzes, namely, the alpha solid solution. These cuts gave microhardness readings which checked with those of copper-tin alloys of the same composition as the alpha solid solution of the leaded bronzes considering the copper and tin only. If the lead and tin had formed a eutectic, enough tin would have been used in this mixture to very appreciably lower the microhardness of the alpha matrix, since the eutectic of lead and tin contains about 60 per cent tin.

During a test of a series of high lead alloys of copper, nickel and lead, it was desired to know the relative hardness of the copper-nickel solution. However, the ordinary hardness testing methods failed to give any information about the separate components of such an alloy. By means of a cut, it was determined that the microhardness of the copper-nickel alloy was 150.

In the shaping of steel parts by screw machines it is important that the metal have good machining quality. The authors have encountered cases where one lot of steel, apparently of exactly the same analysis and Brinell hardness as of the previous lots which had machined satisfactorily, did not cut properly. A microscopic examination of the two steels showed no marked difference. The steels were then microcut giving values of 225 and 250 on the microhardness scale, a difference in cut width of 0.3 of a micron. The steel for which the value was 225 machined well, while the other dulled the tools very rapidly. In another type of steel, where the difference in structure was distinctly discernible under the microscope, the values were 228 and 240. In this case the steel with the higher value machined properly, checking the microscopic observation.

In the study of the case of nitrided and carburized steel, the "microcharacter" lends itself admirably. Continuous readings of microhardness can be made from the extreme edge of the hardened piece to the core and a curve plotted showing the variation of hardness with depth. It can be ascertained from this plot whether the case is uniformly hard, whether it is softer on the surface and exactly how the hardness changes through the section. The microcut will indicate exactly, whether the case is sharp and narrow, or deep and gradually tapering into the core.

It is hoped that this discussion will help other investigators over

some of the rough spots and suggest further research with the "microcharacter" and perhaps indicate how it can be of more practical value.

The authors wish to express their indebtedness to C. H. Bierbaum for his unreserved co-operation, instruction and constructive criticism. Acknowledgment is given to E. P. Langworthy of the Bearium Metals Corp., who was instrumental in supplying much of the material for the research on the alloys studied. Many thanks are extended to Dr. Harold C. Hodge of the University of Rochester Medical School, which unit owns the "microcharacter" used by the authors, for his kind assistance in many instances.

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